Cincinnati University. College of Medicine

TECHNICAL MANUAL
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OF
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I N D E X

GENERAL CHEMISTRY: PROPERTIES OF CHEMICAL WARFARE AGENTS

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MEMORANDUM ON THE PHYSICAL AND CHEMICAL PROPERTIES OF CHEMICAL WARFARE AGENTS,*

C. C. Ruchhoft and Stuart Schott

The term war gas is defined as any chemical agent, solid, liquid or gas, used in warfare for its toxic or irritant action. There is a large number of compounds possessing suitable physiological properties, but certain other properties limit the gases actually suitable for military use to less than two dozen. (†) The important properties required of a war gas may be listed as follows:

(1) Its toxicity should be high, i.e., only a low concentration must be required to produce its poisonous effects.

(2) It must be easily manufactured, and the raw materials necessary in its manufacture must be cheap and available in large quantities.

(3) The gas must be stable enough so that it will not break down on storage or on explosion of the gas shell in which it is fired.

(4) It should be persistent, i.e., remain effective around its point of release for some time.

(5) It should be sufficiently noncorrosive toward metals to permit loading and subsequent storage of gas-filled shells. Besides the above properties, the gas should be insidious, i.e, give no discomfort on first exposure, and it should penetrate masks, protective clothing and other means of gas defense. Considering all of those properties, it is easy to understand that out of 3000 compounds investigated prior to 1918 for possible use as war gases, only 25 to 30 were used in actual combat and only about 6 survived to the end of the last war.

Several systems have been devised for classifying the war gases on the basis of physical, chemical, tactical and physiopathological properties. The physiopathological properties are used in the following classification:

1. Vesicants (Blister Gases) - These include the substances whose characteristic action is to produce blisters on the skin. They exhibit considerable variation in physical and chemical characteristics, the dichlorarsines being in general, less persistent and less stable than mustard gas. These include: dichlordiethyl sulfide (mustard gas), B-chlorvinyldichlorarsine (Lewisite), ethyl and methyl dichlorarsine.

(*) From the National Institute of Health, Division of Public Health Methods. Cincinnati Laboratory.

(†) For a more complete discussion of the elementary principles of military chemistry and chemical agents, the reader is referred to War Department Technical Manual TM 3-215, April 21, 1942.

2. Lung Injurants (Toxic suffocants) - These include those gases which act on the respiratory tract. In general, the members of this group are either true gases or volatile, low boiling liquids. They are nonpersistent. These include: chlorine, phosgene, diphosgene, chloropicrin. As chlorine belongs to the bow and arrow age of chemical warfare, it will be given no more consideration here.

3. Eye Irritants (Lachrymators) - These include those gases having lachrymatory power. They are, for the most part, heavy, oily and relatively high boiling liquids which in the crude state are dark colored owing to decomposition. They are mostly insoluble in water and are very corrosive to metals. Chloracetophenone is a white solid and does not corrode metals. The vapors possess a characteristic but not unpleasant odor. These include xylyl and benzyl bromides, bromacetone, ethyl iodoacetate, brombenzylcyanide, chloracetophenone.

4. Nose Irritants or irritant smokes - Under ordinary conditions these are crystalline solids with negligible vapor pressures. Chemically they are aromatic arsenic derivatives, practically insoluble in water but readily hydrolyzed by alkalies and oxidized by oxidizing agents. These include: diphenyl chlorarsine, diphenylcyanarsine, diphenylamine chlorarsine (Adamsite).

The foregoing classification has defects in that certain gases act differently in changing concentrations and that the biological action of these substances is very complex.

General Properties

The important general properties include vapor pressure, volatility and persistence.

Vapor Pressure - the tendency of all substances to pass into the vapor form causes a certain pressure, called vapor pressure, to be exerted by the vapor produced. The vapor pressure is dependent on the temperature and is usually expressed in mm. of mercury at a specified temperature. This pressure is of special interest for war gases, as the usual toxic substances, in order to be effective, must exert a high enough vapor pressure to supply enough gas to the atmosphere to produce significant physiopathological results. This is of importance for the lachrymators, the vesicants and the lung injurants. In the case of the nose irritants (irritant smokes) the vapor pressure is of minor value as these substances are used in the form of aerosols (colloidal suspensions in the air).

Vapor pressure is a principal factor in the persistence of a gas, that is, the time during which it remains effective at the point of release, the higher the vapor pressure, the less the persistence.

The nonpersistent gases (high vapor pressure) vaporize rapidly when released to form a very concentrated and hence highly toxic cloud, which, however, drifts away with the wind and becomes more or less quickly diluted with the atmosphere. On the other hand, the persistent (low vapor pressure) gases when released, contaminate the surrounding ground,

etc., with liquid which evaporates slowly and continues to give off dangerous vapors for a comparatively long time. It is the persistent gases that make decontamination procedures necessary.

This distinction has an important bearing on the manner in which the gases are used. Both nonpersistent and persistent gases can be used in shells and bombs; only the nonpersistent can be released as clouds from cylinders and only the persistent as spray from aircraft.

The matter of gas identification is affected by the type of gas. With nonpersistent gases, if the gas officer is not on hand immediately when the concentration is very high, the gas will be dispersed by the time he arrives. With persistent gases on the other hand, owing to their lowered vapor pressure, the concentration in the air will never be high, but evidence of ground contamination will be encountered for hours or even days afterward under favorable conditions.

The volatility is defined as the weight of the substance contained in a given volume of saturated air at a certain temperature. Our chemical warfare service expresses volatility in ounces per 1000 cubic feet of air, which is nearly equivalent to mg. per liter.

Neglecting changes in pressure, a simple formula for the volatility is:

$$V_t = \frac{M.W. \times VPt \times 16}{(t + 273)}$$

in which V_t = the volatility at temperature t

MW = the molecular weight of the agent

VP_t = the vapor pressure of the agent at temperature t

t = temperature in degrees Centigrade.

The volatility is one of the most important factors in selecting and evaluating a war gas. In the field it is impossible to reach saturation for the agent. Consequently volatilities as given for the agents in Table 1 may not be obtained. A comparison of the volatilities and the lethal concentrations given in Table 1 indicates which agents might be used effectively for producing casualties.

Vapor Density affects persistence to some extent, the lighter gases having a greater tendency to rise and be dispersed whereas the heavier gases tend to hug the ground. The war gases mentioned here vary in vapor density from 2.5 for chlorine to 7.4 for ethyliodoacetate.

Freezing Point is not important except for mustard gas (14.4°C) and for brombenzylcyanide (25.5°C). These gases are usually diluted with 15-20% of carbon tetrachloride or chlorobenzene to lower the freezing point.

In connection with freezing point, reference should be made to the war "gases" which are really solids (chloracetophenone, m.p. 58° C and arsenical nose irritants m.p. from 32° to 195° C). The latter substances, in particular, have very low vapor pressures and would be useless as war gases except for the fact that they can be dispersed by heat, etc., in form of a "smoke" or particulate cloud, consisting of very small particles (about 10^{-4} to 10^{-5} mm. diameter) suspended in the atmosphere and capable of exerting an irritant action on the nose and throat. The action is similar with chloracetophenone, although its vapor alone will cause irritation.

These clouds are classified as nonpersistent since they are rapidly dissipated by the wind as are the true nonpersistent gases. Special type of bombs and thermogenerators have been devised for their employment in warfare. They were originally designed as "mask breakers," the particles not being absorbed by activated charcoal as are vapors but necessitating the use of special filters. This aspect is of importance in their detection; they cannot be satisfactorily sampled by the usual technique of absorption in solvents, but require a suitable filter. At the same time they are effective in exceedingly low concentrations and are nonpersistent so that the prospect of obtaining an analyzable sample is usually remote.

Stability - Of the chemical properties, reaction with water is of prime importance, particularly the persistence under wet conditions. Most of the gases are relatively insoluble in water; some, such as chloropicrin, are practically unaffected by it; others, like mustard gas, are slowly hydrolyzed; while still others, e.g., phosgene and lewisite, are rapidly decomposed. This means that lewisite would be relatively ineffective in rainy weather and the persistence of mustard gas would be considerably reduced.

From the tactical viewpoint, the stability of gases to heat and explosion and their action on metals are of importance. From the standpoint of defense the behavior toward neutralizing agents such as alkalies and oxidizing agents is of importance.

Physical and Chemical Properties

1. Lung Injurants

(a) Phosgene (C.G.) (Carbonyl Chloride: $COCl_2$). At ordinary temperature phosgene is a colorless gas with a characteristic odor described as that of moldy hay. It was first used in war by Germans in December, 1915, and remained the principal war gas throughout the first world war.

It condenses on cooling below 8°C to a colorless liquid if pure; to a pale yellow or orange if the technical product. The gas is approximately three and a half times as heavy as air. However, due to its high vapor pressure (low boiling point) it is a very nonpersistent gas.

Phosgene is readily soluble in many organic solvents, benzene, toluene, xylene, fats and oils, inorganic halides such as those of arsenic and sulfur. Phosgene is very soluble in water but is hydrolyzed with extreme rapidity to carbon dioxide and hydrochloric acid. Like all acid chlorides, phosgene is very reactive, reacting readily with alkalies, alcohols, phenols and amines. The reaction with phenols and amine was utilized in the old type PH gas helmet which was impregnated with sodium phenate and hexamine. Phosgene is noncorrosive toward metals when dry but extremely corrosive when moist.

(b) Diphosgene (Trichlormethyl chloroformate: $ClCOOCCl_3$), known to the French as Surpalite and to the Germans as Perstoff, was one of the principal lethal gases used in the last war and was used in shells. Diphosgene boils at 128° C and has a specific gravity of 1.65 at 15° C. Its vapor density is 6.9 and its vapor pressure at 20° C is 10.3 mm., so that it is still a nonpersistent gas although it is more persistent than chlorine or phosgene. The vapor has an odor similar to that of phosgene although more pungent. With heat it decomposes to form two molecules of phosgene and reacts with water and amines as if consisting of two molecules of phosgene. When dry it is noncorrosive to metals.

(c) Chloropicrin (P.S.) (Trichloronitromethane, CCl_3NO_2), known as "Klop" to the Germans, as Aquinite to the French and sometimes as vomiting gas to the British, was first used by Russians in hand grenades dissolved in 50% sulfuryl chloride in 1916 and was later employed by the Allies as a constituent of their penetrating NC mixture (80% chloropicrin plus 20% stannic chloride).

Chloropicrin in the pure state is a slightly oily, colorless, refractive liquid with a characteristic odor. The crude product is yellow due to impurities. It boils at 112° at ordinary pressure and has a density of 1.66. Its vapor density is 5.69 and vapor pressure 18.3 mm. at 20° C, so that it is relatively nonpersistent. The vapor has a sweetish odor and distinct lachrymatory properties. It is relatively insoluble in water but soluble in organic solvents. It is fairly stable, not being hydrolyzed by water nor affected by ordinary acids or alkalies. Alcoholic sodium hydroxide gradually decomposes it, as do also sodium sulfite and alkaline polysulfides. It is partially dissociated on heating into nitrosyl chloride and phosgene and may explode on rapid heating. When moist it is corrosive toward metals, but produces only a superficial stain which forms a protective layer.

2. Lachrymators

Xylyl Bromide (German T-staff) (CH_3-C_6H_4-CH_2-Br). A crude mixture of o-, m- and p-xylyl bromides obtained by bromination of xylene used extensively as a lachrymatory shell-filling by the Germans. It was used for the first time as a war gas in January, 1915, (Sartori), but its use was abandoned toward the end of the war because of the ease with which it was dealt by ordinary carbon filters and of the inconvenience caused by its attack on iron containers. The mixture is a black liquid, density 1.4 and B.P. 210-222° C. It is persistent (vapor pressure about 0.07 mm. at 20° C), and its heavy vapors when diluted

have an odor resembling lilacs or elder blossoms or leaves, hence the British wartime name of Elder-gas. It is insoluble in and slowly decomposed by water but is readily hydrolyzed by alkalies.

Benzyl bromide (C_6H_5 CH_2 Br) (B.P. 200° C, D., 1.44, vapor density is 5.8), called "cyclite" by French. First used by the Germans in March, 1915, but only for a short time due to the cost and scarcity of the raw material, toluene. Later it was completely abandoned, being superseded by other substances with greater irritant power.

Bromacetone (CH_3 $COCH_2$ Br), obtained by bromination of acetone, was used by the Germans as B-Stoff, and by the French, in 80/20 admixture with chloracetone as Martonite. Pure bromacetone is a colorless liquid with a pungent odor (BP. 136° C, D = 1.6, vapor density = 4.75). It is relatively volatile (vapor pressure at 20° = 9 mm.) and toxic concentrations of its vapors may be met in the field. The liquid is slightly soluble in water, very soluble in organic solvents. It is not very stable, tending to polymerize to a resin under the influence of light and heat, although this action may be delayed for several months by addition of a stabilizer such as magnesium oxide. It attacks iron but not lead.

Ethyl iodoacetate (English K.S.K.) ($CH_2ICOOC_2H_5$) used solely by the British, especially in mixtures with 10% chloropicrin. It is a colorless dense liquid boiling at 179° C and having a density of 1.8, vapor pressure 0.54 mm. at 20° C and a vapor density of 7.4. Thus it is a relatively persistent substance. It is insoluble in, and stable to water and is only slowly hydrolyzed by hot aqueous alkali. It reacts with alcoholic alkali and sodium thiosulfate and is decomposed by hot nitric acid. It is corrosive to metals.

Brombenzylcyanide (C.A.) (C_6H_5CHBr-CN) was experimentally tried out towards the end of the war and according to American post-war experiments it is one of the most efficient war gases because of its high lachrymatory power. When pure it consists of yellowish-white crystals which slowly turn red on decomposition. It has a M.P. of 25.5° C, B.P. 242° C, D = 1.52, vapor density = 6.8, vapor pressure = 0.012 mm. at 20° C. The liquid is accordingly very persistent. It is insoluble in water, but dissolves easily in many organic solvents. It is highly resistant to chemical and atmospheric agencies. Water and humidity decompose it only very slowly. Cold sodium hydroxide acts similarly, but it is hydrolyzed by alcoholic alkali in the cold. It has the undesirable property of vigorously attacking all the common metals except lead and in doing so its lachrymatory properties are destroyed. Containers holding this compound must be lined with glass, lead or rubber. Another limitation is its low stability to the shock of the bursting projectile. It can only be employed in bombs with a comparatively small bursting charge.

Chloracetophenone (CN) ($C_6H_5COCH_2Cl$). This compound, because of its lachrymatory properties, was tested during the last war at Edgewood Arsenal. It is a white crystalline solid, m.p. 58° C, B.P. 244-45°, vapor pressure 0.0198 mm. at 25° C, with a pleasant aromatic odor resembling that of apple blossoms. As a chemical warfare agent it is dispersed by heat in the form of a nonpersistent particulate cloud.

It is practically insoluble in water (about 0.1% at ordinary temperature) but soluble in most organic solvents. The solubility of Chloracetophenone in readily volatile solvents may be utilized in diffusing it into the air. For this purpose benzene is the best solvent, carbon tetrachloride also being occasionally employed. When a solution in one of these solvents is sprayed into the air the solvent evaporates rapidly, leaving the chloracetophenone dispersed in a fine state of subdivision. (It is very effective when distilled into the air by the heat of a burning composition, e.g., a mixture of CN with small-grained smokeless powder). It is a stable compound, unaffected by boiling water, but the chlorine is readily removed by alkaline hydrolysis. It does not attack iron and is insensitive to heat and detonation.

Nose irritants (irritant smokes)

The action of these compounds, of an aromatic arsenical nature, is provoked by finely divided solid particles which on liberation in the air form true smokes and are known as the toxic smokes. They were intended as "mask breakers" but were not very successful in this respect because their use in modified high explosive shells did not give a good particulate cloud. When released as a cloud from smoke candles they are very effective. Under ordinary conditions they are crystalline solids with negligible vapor pressure.

Diphenylchlorarsine (D.S.) ($(C_6H_5)_2AsCl$) German "Clark I." The crude material is a dark brown liquid which gradually turns into a semisolid viscous mass. The pure material forms colorless crystals melting at 41° C, B.P. 333°, vapor pressure 0.0005 mm. at 20°. It is only slightly soluble in water but soluble in some organic solvents. Water hydrolyzes it very slowly and aqueous and alcoholic alkali react rapidly. It is insensitive to heat and detonation and does not corrode iron or steel.

Diphenylcyanarsine (CDA) ($(C_6H_5)_2$ AsCN) German Clark II - Employed as war gas toward the end of the last war (May, 1918) both alone and mixed with diphenylchlorarsine. It forms colorless prisms with an odor of mixed garlic and bitter almonds. M.P. 35° C, sparingly soluble in water but dissolves in some organic solvents. Its properties are similar to that of the chlor derivative, being employed in the same manner but effective at a lower concentration.

Diphenylaminechlorarsine (D.M.) ($NH(C_6H_4)_2$:AsCl) also called "phenarsazine chloride" and "Adamsite." In the crude state is a crystalline solid, the pure product being a yellow, odorless solid, M.P. 195° C. It is practically insoluble in water and sparingly soluble in common organic solvents. Phenarsazine chloride, unlike the chlor and cyano arsine mentioned above, is slowly hydrolyzed by water. It is readily hydrolyzed by alkalies, and oxidized by oxidizing agents. Iron, steel, bronze and copper are corroded by this compound.

Vesicants

Mustard gas is the chief member of this group, and was the only one used to any extent during the last war, although the potentialities of lewisite and other dichlorarsines were being investigated at the end

of the last war. These compounds show considerable variation in physical and chemical properties; the dichlorarsines being, in general, less persistent and less stable than mustard. They all possess the common characteristic of being able to penetrate into and destroy all living tissues which they contact.

Mustard gas (H.S.) (2,2' dichlorodiethyl sulfide, $S(CH_2CH_2Cl)_2$, known to the French as "Yperite" and to the Germans as "Senfgas" or "Lost." First employed by the Germans in July, 1917. In the pure state, mustard gas is a colorless oily liquid having a faint leek-like odor, D=1.28. B.P. 217.5° C, M.P. 14.4°C. In the crude state it is brown and has an odor reminiscent of mustard. The vapor pressure is 0.115 mm. at 20° and its vapor density 5.4, so that it is very persistent, especially on terrain covered with bushes and shrubs. The technical product containing 15-20% of carbon tetrachloride or chlorobenzene is a brown or black oil, (freezing point about 5° C) having a characteristic odor described as resembling that of mustard, garlic or horseradish.

It is sparingly soluble in water (about 0.06% at ordinary temperatures) in which it sinks. It is slowly hydrolyzed to give harmless water soluble products.

$$S(CH_2CH_2Cl)_2 + 2\ H_2O \longrightarrow \underset{\text{thiodiglycol}}{\underline{S(CH_2CH_2OH)_2}} + 2\ HCl$$

The following values have been determined for the hydrolysis of mustard gas.

Time (Minutes)	Per cent hydrolyzed compared to that dissolved
10	50
20	70
30	79
40	84
50	85
60	85

The velocity is influenced by time of contact, temperature, water-mustard gas ratio, quantities of acid, alkali and hydrolysis products present and the degree of dispersion in water. In the presence of a large excess of water the above conversion is quantitative.

Dry chloride of lime reacts with mustard gas acting as an oxidant and chlorinating agent. A very violent reaction, with evolution of heat, flame and white vapors, takes place. Numerous compounds are formed, carbon dioxide, hydrochloric acid, chloral and chlorinated substances which are not defined. By the action of chloride of lime mixed with water, the action is less violent and this type of mixture is employed for decontamination of objects contaminated with mustard gas. This action of the bleaching powder depends on its available chlorine and the bleach should contain at least 15% active chlorine.

The pure liquid does not attack metals under ordinary conditions but the technical product usually contains free hydrochloric acid and has a marked corrosive action on iron and steel.

Lewisite (M-1) (Betachlorovinyl dichlorarsine, $Cl-CH = CHAsCl_2$) was developed as a war gas by the Americans during the last war but was never used in the field. It has been termed the "Dew of Death," and is claimed to embody the aggressive qualities of the asphyxiants, the irritant characteristics of the tear and nose irritant gases and the universal action on all tissues of the blister gases.

When pure, lewisite is a colorless liquid (B.P. 190°, with decomposition), M.P. about 0° C, vapor pressure 0.4 mm. at 20° (less persistent than mustard). The vapor of the pure compound has an irritant action on the eyes and nose. The liquid tends to turn blue-black in the light. The technical product, which is usually black, has an intolerable geranium-like odor, perceptible in great dilution.

Lewisite is sparingly soluble in water about 0.05%, but readily soluble in organic solvents. It is rapidly hydrolyzed by water or even a damp atmosphere at ordinary temperatures.

$$Cl-CH=CH-As\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + H_2O \longrightarrow 2HCl + \underset{\text{chlorvinyl arsenious oxide}}{Cl-CH=CHAs=O}$$

Chlorvinylarsenious oxide is somewhat vesicant for direct contact but is much less dangerous than lewisite because it is nonvolatile, and sparingly soluble in water and other solvents. This hydrolysis is notably increased by an increase in temperature. Alkalies (except ammonia) completely decompose the molecule into acetylene and sodium arsenite:

$$Cl\ CH = CH-AsCl_2 + 6NaOH \longrightarrow Na_3AsO_3 + 3\ NaCl + C_2H_2 + 3\ H_2O$$

When a 15% NaOH solution is employed at temperatures below 37° C, this decomposition takes place quantitatively, and only in the case of beta chlorvinyldichlorarsine.

Lewisite is very reactive, being readily oxidized (hydrogen peroxide) and chlorinated; the two chlorine atoms are replaceable by treatment with potassium iodide, hydrogen sulfide, etc. It does not attack steel appreciably and when stored in projectiles causes only a slight superficial rusting of the metal walls.

Ethyl dichlorarsine (ED) ($C_2H_5AsCl_2$)

This compound was employed in March, 1918, by the Germans, being considered suitable for replacing mustard gas in offensive operations because of its immediate vesicant effect and its nonpersistent character. It is a mobile liquid, fruity odor in dilution, (odor can be detected when concentration is 0.5 mgm. (cu. m. of air), B.P. 156° C vapor density 6, vapor pressure at 21.5° C is 2.29 mm. It is readily soluble in organic solvents and dissolves to the extent of 0.1% in water.

Water rapidly hydrolyzes ethyl dichlorarsine:

$$C_2H_5AsCl_2 + 2H_2O \rightarrow C_2H_5AsO + 2HCl$$

The compound also reacts with sodium iodide to give the iodo derivative, with hydrogen sulfide to give the sulfide and is decomposed readily by bleaching powder which is used in decontamination. When dry it does not attack iron but it corrodes brass strongly.

Methyl dichlorarsine (MD) CH_3AsCl_2 is a mobile colorless liquid which does not fume in the air. B.P. 132-33° C, vapor density 5.5, vapor pressure 10.8 at 25° C. Its properties are similar to those of the ethyl derivative.

TABLE 1

PROPERTIES OF CHEMICAL WARFARE AGENTS

PROPERTY	VESICANTS			LUNG INJURANT		LACRIMATORS	
Common Name	Mustard	Lewisite	Ethyl-dichlor-arsine	Phosgene	Chlorpicrin	Brombenzyl-cyanide	Chlor-aceto-phenone
Chemical Name	Dichlor ethyl-sulfide	B-chlor-vinyl Di-chlorarsine	" "	Carbonyl-chloride	Trichlor-nitromethane	" "	" "
Symbol (U. S.)	HS	M-1	ED	CG	PS	CA	CN
Melting Point	14°C. 57°F.	-18.2°C. 0°F.	-30°C. -22°F.	-118°C. -190°F.	-69.2°C. -92.4°F.	25°C. 77°F.	59°C. 138°F.
Boiling Point	217°C. 422.6°F.	190°C. 374°F.	156°C. 312°F.	8.2°C. 46.7°F.	112°C. 231.5°F.	225°C. 437°F.	247°C. 476°F.
Vapor Density (Air = 1)	5.5	7.1	6.5	3.5	5.6	6.6	5.2
Vapor Pressure (mm. Hg. at 20°C.)	0.065	0.395	5.0	1180	18.3	0.0112	0.013
Volatility (Oz. per 1000 cu. ft.)	0.625	4.5	100	4420	165	0.13	0.106
Lethal Concentration (Oz. per 1000 cu. ft.) 10 minute Exposure	0.15	0.12	0.50	0.50	2.0	3.5	0.85
Persistency, summer	1 - 7 days	1 - 7 days	1 - 6 hrs.	3 - 10 min.	1 - 4 hrs.	3 - 7 days	10 min.
Persistency, winter	Several weeks	1 week	2-12 hrs.	20 min. to 2 hours	1/2 - 7 days	Several weeks	10 min.
Solvents for	Oils PS Ethanol CCl_4	HS - PS Oils Ethanol	Ethyl chloride	Cl PS	$CHCl_3$, CG Cl, CS_2 C_6H_6 C_2H_5OH	C_6H_5Cl, $CHCl_3$, PS, CG	$CHCl_3$, PS Ethylene dichlorid chlor-acetone

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TABLE 1 (Continued)

PROPERTIES OF CHEMICAL WARFARE AGENTS.

PROPERTY	IRRITANT SMOKES			SCREENING SMOKES		
Common name	Adamsite	Diphenyl-chlorarsine	Diphenyl-cyanoarsine	HC Mixture	Titanium tetrachloride	Sulfur trioxide solution
Chemical Name	Diphenyl-amine chlor-arsine	" "	" "	Hexachlor-ethane + Zn + ZnO	" "	SO_3 Chlor-Sulfonic Acid
Symbol (U. S.)	DM	DA	CDA	HC	FM	FS
Melting Point	195°C. 387°F.	45°C. 113°F.	31.5°C. 91°F.	184°C. 363°F.	-23°C. -9°F.	Below -30°C. -22°F.
Boiling Point	410°C. 770°F.	383°C. 720°F.	350°C. 662°F.	185°C. 365°F.	136°C. 277°F.	--- ---
Vapor Density (Air = 1)	---	---	---	Negligible	---	---
Vapor Pressure (mm. Hg. at 20°C.)	Negligible	0.0005	0.0001	0.22	8.32	---
Volatility (Oz. per 1000 cu. ft.)	" "	0.0007	0.0015	2.85	8.64	---
Lethal Concentration (Oz. per 1000 cu. ft.)	10 Minute Exposure 3.0	1.5	1.0	---- Smoke Harmless		---
Persistency, summer	10 min.	10 min.	10 min.	Only while burning	10 min.	While container is operating
Persistency, winter	10 min.	10 min.	10 min.	" "	10 min.	" "
Solvents for	Furfural acetone	Acetone $CHCl_3$, PS	Organic Solvents	Alcohol and Ether for hexachlor-ethane	Ethylene dichloride	Strong Sulfuric acid

TABLE 2

TACTICAL AND PHYSIOLOGICAL CLASSIFICATION OF COMMON CHEMICAL WARFARE AGENTS

Agent	Persistency	Tactical Classes - C.W.S. Markings				Physiological Classification			
		Casualty	Harassing	Screening	Incendiary	Vesicant	Lung Injurant	Lacrimator	Irritant*
Mustard	Highly persistent	HS Gas	HS Gas			D			
Lewisite	Persistent	M-1 Gas	M-1 Gas			D			
Ethyl di-chlorarsine	Moderately Persistent	ED Gas	ED Gas			D			I
Phosgene	Non-persistent	CG Gas					ID		
Chlorpicrin	Moderately Persistent	PS Gas	PS Gas				D	I	
Brom benzyl cyanide	Highly persistent		CA Gas					I	
Chloraceto phenone	Non-persistent		CN Gas					I	
CN Solution	" " "		CNS Gas					I	
Adamsite	" " "		DM Gas						I
Sulfur trioxide solution				FS Smoke					
HC Mixture	Non-persistent			HC Smoke					
White Phosphorus	" " "	WP Smoke		WP Smoke	WP Smoke				
Thermit					TH Smoke				

Legend: [solid box] Primary Classification
[dashed box] Secondary Classification
* Other than lacrimators

I = Immediate Action
D = Delayed Action
ID = Immediate to Delayed Action

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MEMORANDUM ON METHODS FOR THE DETECTION OF CHEMICAL WARFARE GASES*

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The detection of the presence of war gases along with the identification of the gas plays a very important role in defense. In case of gas attack it is vital to know quickly the nature of the gas used and the extent of the areas affected and for this reason the methods for detection of gases must possess the following properties:

1. Results should be accurate and readily obtainable.

   (a) The tests should be of a simple nature requiring no complex manipulation.

   (b) The equipment necessary should be simple and preferably usable in the field.

   (c) The test should be sensitive so that small traces of the gases may be identified.

2. The method should be reasonably specific, i.e. give a typical result for only one gas.

The British field kit contains simple apparatus for the detection of mustard gas and equipment for taking contaminated samples of material for subsequent examination, also detector paper for delineation of contaminated areas and means for sampling vapors and particulate clouds. They consider mustard gas the principal subject for their work and depend on subjective methods for the others in the field, or on subsequent laboratory examination.

In the case of non-persistent gases and particulate clouds, little action is possible unless the gas officer is present at the time of release; otherwise by the time of arrival the gas is too dilute for identification. With bombs containing the less volatile but still non-persistent lung irritants, such as diphosgene and chloropicrin, it will usually be possible to detect the gas in the earth surrounding the bomb crater for hours afterward.

Of the persistent gases, the persistent lachrymators are identified by lachrymation. As mentioned above, the persistent vesicants, on the other hand, particularly mustard gas, are the main reason for the Gas Identification Service in Britain. Rapid detection of the blister gases is essential to avoid spreading of contamination from the gas bomb and to enable prompt decontamination measures to be started.

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* From Division of Public Health Methods, National Institute of Health.

Two general methods of gas detection are available and used, these being the subjective and objective. Subjective tests include smell, appearance and physiological action. Objective tests include physical and chemical methods.

For speedy recognition in the field the subjective tests are very rapid and are normally of great value. The objective tests are, however, very useful for actual identification and for confirmation of the subjective tests.

SUBJECTIVE METHOD

1. SMELL - Many of the war gases have definite odors that can be detected in relatively harmless concentrations. Crude mustard gas can be detected by smell in a concentration of 1 in 20,000,000 (approx. 0.35 mg. per cu. m. of air), and the geranium-like odor of lewisite can be detected in even greater dilutions.

The sense of smell has certain limitations. It is liable to be erratic, subject to personal idiosyncrasy and individual variation in different individuals, and from time to time in the same individual.

In spite of the objections noted in the preceding paragraph, the sense of smell is very useful and can be developed by practice with odor kits. These are a collection of samples of war gases suitably contained (usually absorbed on activated carbon in a bottle) by which one may thoroughly acquaint himself with the characteristic odors of certain war gases.

Certain rules should be followed in making odor tests:

(1) Don't inhale deeply.

(2) Smell only once; repeated smelling dulls perception.

(3) First smell and then think; the ability to recall smells can be acquired by practice.

(4) After smelling breathe out strongly through the nose several times.

*(5) Don't smoke while smelling; smoking dulls the sense of smell.

*Even slight traces of phosgene affects the taste nerves so that tobacco smoke acquires a flat, metallic taste and becomes disagreeable and repugnant. Hydrocyanic acid and hydrogen sulfide have the same reaction to a lesser degree.

(6) Name each odor perception. A gas is odorless only when no odor is evident. In the event of an unfamiliar smell, it is important that the description of the odor be accurate and comprehensive.

Smell tests in the field should be made downwind -- when wearing a respirator by turning the back of the head to the wind and inserting the fingers between the facepiece and the cheek and sniffing gently. The tendency of gases and vapors to rise as they drift downward should also be borne in mind and care taken to make smell tests close to the ground when endeavoring to locate the source of contamination.

SIGHT

The sense of sight is of importance in the recognition of persistent gases. Certain cases of non-persistent gases may be mentioned; e.g., a concentrated cloud of chlorine has the characteristic yellow green color of this element unless there is much moisture in the atmosphere, when it appears whitish owing to condensation. Phosgene and diphosgene similarly give whitish clouds under damp conditions but are invisible when dry; particulate arsenic "smokes" are white and opaque if sufficiently concentrated. A white cloud does not always indicate poison gas; it may be screening smoke or smoke arising from use of incendiary or other bombs.

In general, the non-persistent gases will have been dissipated before the gas officers arrive, leaving a certain amount of residual evidence in the form of rotted clothing and bleached vegetation, or corroded metals, particularly copper and copper alloys (notably with the lung irritants in damp weather). The size of the bomb crater may indicate gas, as craters produced by high explosive bombs are usually considerably deeper and more extensive than those from gas bombs.

With the persistent gases on the other hand, and mustard gas in particular, sight may or may not afford a reliable indication according to circumstances, but contamination of grounds and building with the liquid gas will invariably occur and afford visual evidence.

Contamination by crude mustard gas, which has a black color, is somewhat easier to detect than that of the pure pale yellow product, although the stains have the same appearance other than their color. On dry porous surfaces the liquid is rapidly absorbed, leaving a dark oily stain. On dry roads and dry earth it also appears as a dark oily patch, while on wet surfaces it spreads and gives a slight iridescent effect. It remains as liquid drops and splashes on painted surfaces for a considerable time although it eventually softens and dissolves in the film. It does not penetrate into metals, glazed tiles and other impermeable materials and also remains in droplet form on green foliage and grass for some time, eventually penetrating and damaging vegetation. In water, the bulk settles to the bottom, but a thin and somewhat iridescent film usually remains on the surface for some time.

The indications above noted are applicable to the immediate vicinity of the bomb crater. Lighter contamination further away and resulting from aerial spray takes the form of very small pinpoint droplets and is harder to see.

The crude blister gases are similar in appearance to the persistent lachrymators (both dark colored oils) and the two may be confused. Periodic smelling tests should be made to avoid this confusion.

Physiological action forms a valuable adjunct in the identification of some gases. Lachrymators are readily recognized by their immediate irritant effects on the eyes even in low concentrations (1 in 20-30 million). Similarly the nose irritants give rise to their characteristic, though slightly delayed, irritation of the nose, throat and chest even in low concentrations. With those smokes which are practically odorless in such dilutions, physiological detection becomes the only practicable field method.

Of the lung irritants, chloropicrin has lachrymatory effects in relatively low concentrations and like chlorine is intolerable to breathe in concentrations which are relatively harmless. With phosgene and diphosgene, on the other hand, the irritant effects are far less marked, and concentrations which are just detectable by smell and slight irritation of the breathing passages are not intolerable to breathe, but may lead to serious results if breathed for any length of time. Further, the intensity of physiological effects afford little indication of the concentration present. To wait for physiological indications in the case of such gases is inviting disaster.

Similar remarks apply especially to mustard gas, which has a characteristic delayed action and produces no immediately recognizable symptoms. The arsenical vesicants, lewisite, etc., have an immediate irritant effect on the nose and eyes which can serve as a warning indication.

The use of test animals is of value in certain circumstances but has obvious limitations and is not suitable for general war application.

OBJECTIVE METHODS

The majority of these methods fail to fulfill the four essential requirements of simplicity, rapidity, specificity and sensitivity.

PHYSICAL AND PHYSICO - CHEMICAL METHODS

On the physical side, various methods depending on altered physical properties (refractive index, rate of diffusion, electrical conductivity, etc.) have been suggested but all these methods are non-specific, merely indicating the presence of impurity in the air. Moreover, the apparatus is cumbersome.

The proposed physico-chemical methods meet similar objections. Spectrographic work is specific and sensitive but is not suitable for field work. The Beilstein flame test is useful for detecting halogens but is not specific.

For assisting in delineation of areas contaminated with vesicants, indicators have been devised known as "Detectors, Ground", consisting of paper or other material painted with special yellow colored paint which turns red in contact with the liquid gas.

Several objections arise, namely, that the paint is not specific for blister gases, a positive reaction is only given by liquid contamination, and a coloration is not always easily perceptible in case of the crude gases. A similar type of detector is valuable in cases of airplane spray of persistent gases.

CHEMICAL METHODS

Chemical methods depend on the formation of insoluble or highly colored compounds by reaction of the gases with a particular agent.

As many gases contain a hydrolyzable halogen, the simplest, but least specific, is the test for free acidity by means of a pad impregnated with methyl red pressed into contact with the suspected materials, or bubbling the suspected air through a neutral unbuffered water containing brom thymol blue indicator. The S.D.C. portable pH kit containing a spot plate and the necessary indicators is very useful for detecting free acidity. This method holds only for those gases readily hydrolyzable and is affected by any extraneous gases present in the atmosphere in the case of the air sampling test.

In the same way and subject to the same limitations, the gases may be passed through alcoholic silver nitrate and the presence of readily hydrolyzable halogen containing war gases detected.

The ideal chemical method is one depending on the color change of an impregnated paper. For certain industrial gases this method is feasible, but for the majority of war gases paper tests either are not available or are not sufficiently sensitive or specific. The Chemical Warfare Service has at present a very satisfactory detector set which will detect vesicants in the liquid state and is also specific for mustard gas in the vapor state. The Chemical Warfare Service is working to perfect and expand the set so that it will be more sensitive to vapor and so that it will show the presence of new suspected German gases. Another device which has recently been developed contains finely divided charcoal deposited in the mesh of a fine copper screen. If the presence of a war gas is suspected the screen is waved in the air and then placed in a hot flame. Part of the gas is absorbed on the charcoal and subsequently decomposed in the flame. Since many of the chemical warfare agents contain halogens a green flame on the screen indicates the presence of such a gas. In the absence of such detectors one must resort to passing the suspected air through a suitable solvent or absorbent (a filter in case of the particulate clouds) and applying the reaction to the latter. This general method, despite obvious defects, is of value in gas identification as it enables the gas to be stored up in an artificially concentrated condition and if required, taken away to the laboratory for identification.

Chemical methods can give accurate and definite information, but few of these can be described as rapid and simple and their application in the field may be questionable on account of the amount of apparatus and reagents involved.

Collection of Samples

Guided by subjective indications as to the general type of gas the samples collected may be:

1. Air samples of non-persistent gases taken with an activated carbon tube using the hand pump.*

2. Samples of particulate clouds taken with a cotton wool filter using the hand pump.

3. Samples of material contaminated with persistent and semi-persistent gases - earth, plaster, drops absorbed on filter paper, etc.

Examination of the Samples

In the subsequent chemical examination of such samples to establish or confirm the identity of the gas present, the following general procedure should be employed.

1. Non-persistent gases and particulate clouds

Samples of these will normally not be available, but if taken the examination should be along the following lines:

(a) Filter - Either examine as a whole for arsenic; or if a reasonable amount of particulate matter has been collected, extract with hot alcohol, and either examine the extract for suspected compounds or evaporate the extract and examine the residue for m.p., elements, or specific compounds.

(b) Charcoal - The carbon granules may be examined for the elements. The gas absorbed on granules may be hydrolyzed by alcoholic potash and filtered and the filtrate examined for halides, nitrites and other products of hydrolysis.

2. Persistent and semi-persistent gases

The sample bottles should be opened in a hood and the examination carried out for:

(a) Persistent lachrymators. If the gas appears to be a lachrymator from its subjective properties, a portion of the sample should be extracted with alcohol. The filtered alcohol extract may be hydrolyzed by warming

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* Diagrams indicating common simple gas sampling devices are given in the appendix.

with alcoholic potassium hydroxide and the resultant solution examined for the lachrymators. Certain tests should be made on the unhydrolyzed alcoholic extract as noted under "Chemical Methods".

(b) Other gases -- If the presence of other gases is indicated or suspected, the bottle should be fitted with a two hole rubber stopper carrying two glass tubes. By means of this arrangement air is aspirated over the sample. The effluent air stream may be passed through alcoholic potash, and this solution after acidification tested for halides and cyanides, nitrite and arsenite. The results of these preliminary experiments may be confirmed by aspirating the effluent air successively through reagents (one at a time) giving characteristic tests for certain gases; e.g., the aniline reaction for diphosgene, the gold chloride and iodoplatinate test for mustard, the acetylene test for lewisite, etc.

The air flow analysis described in the preceding paragraph is in general the simplest, safest and most satisfactory method for examining samples of contaminated materials.

With this method, using reaction bubblers of simple type, the air should be aspirated relatively slowly (up to about 500 cc. per minute) and if the sample is only lightly contaminated it is best to surround the sample bottle with warm water to increase the volatility of the gas. The influent air should be purified by passage through an activated carbon tube and a calcium chloride tube; as far as possible all joints should be glass to glass to avoid absorption of gases such as phosgene, chlorpicrin and mustard gas by rubber connections.

Within limits the sensitivity of these reactions can be artificially increased and the time taken for analysis reduced by use of higher rates of flow with bubblers that break up the influent air stream to some extent.

A rough indication of the degree of contamination is obtained from the intensity of the reaction obtained.

VESICANTS

Mustard Gas - (HS) dichlordiethyl-sulfide $[(ClCH_2CH_2)_2S]$

Yablich's Reagent

This reagent was suggested by the Chemical Warfare Service and was especially employed by the Americans in the last war.

When air containing mustard is passed through a solution of selenious acid in dilute sulfuric acid and the reagent then heated for 10 minutes at 85° C. a yellow precipitate of metallic selenium is produced. If the amount of dichloroethyl sulfide present is small, a reddish orange suspension appears. The reagent is prepared by dissolving 1 gm. SeO_2 in 100 ml of a solution containing equal parts by weight of sulfuric acid and water.

Although many war gases give a negative reaction with this reagent, all of the arsine derivatives give as positive a result as mustard. A similar reaction is also given by carbon monoxide and hydrogen sulfide. Sensitivity -- 5 mgm mustard per cubic meter of air.

Grignard's Reagent

This reagent, which is fairly specific for mustard, was proposed by Grignard in 1918 but was kept secret until 1921. Detection is based on the following double decomposition:

$$S(C_2H_4Cl)_2 + 2HI \longrightarrow S(C_2H_4I)_2 + 2HCl$$

The dichloroethyl sulfide is converted to diiodo-ethyl sulfide which separates as yellow crystals.

PREPARATION OF REAGENT

Sodium Iodide	2 gm.
7.5% copper sulfate solution	40 drops
35% gum arabic solution	2 ml.
Water	200 ml.

The copper sulfate is added to catalyze the reaction while the gum arabic causes the diiodo-ethyl sulfide to separate in the colloidal form.

For the detection of mustard, the air under examination is passed through the above reagent and in the presence of mustard a yellow precipitate appears. 100 mgm of mustard may be detected in 1 cu. meter of air in 4 minutes. The British say that 0.025 mgm / ml. solution may be detected.

It was found that while the aliphatic arsines and phenylcarbylamines produce a similar turbidity at high concentrations (4%) other substances such as mono-, di-, and trichloromethyl chloroformates, chloropicrin, benzyl bromide, acrolein, the aromatic arsines, thiodiglycol, etc., do not react.

Schroter's Method

This is based on the property of mustard gas forming additive compounds with gold and palladium chlorides.

On treating with mustard an aqueous solution containing 0.1% gold chloride or 0.05% palladium chloride a turbidity of colloidal type quickly forms, and if the quantity of the sulfide is large, yellowish-red oily droplets are produced.

This reaction may be carried out on filter paper. In this case a reddish brown stain is formed with a 10% gold chloride solution and a yellow stain with a 0.2% palladium chloride solution.

These reagents are supposedly specific for mustard gas and are not influenced by the presence of any other war gas, nor by the hydrolysis products of mustard.

The sensitivity with gold chloride is of the order of 10 mgm. mustard gas per cu. m. of air. The British give the sensitivity as 0.075 mgm. per ml. solution.

An apparatus has been designed for detecting presence of mustard in a sample of air by this reaction. The air is drawn by means of a small pump through a glass tube containing silica gel, to which are added after a certain number of strokes of the pump, several drops of gold chloride solution. A little more air is drawn through the tube and then a few drops of hydrogen peroxide are added.

In the presence of mustard a yellow ring forms.

Sensitivity: 12 mgm. of mustard per cubic meter of air.

Iodoplatinate Test

This test depends on the reduction of platinic chloride to platinous chloride with the liberation of free iodine.

The mustard gas vapor is removed from the contaminated sample by passage through glass wool moistened with 5% acetic acid, followed by addition of several drops of the iodoplatinate reagent to the glass wool followed by two drops of the starch reagent. On shaking the sampling tube a blue color appears if mustard gas is present or rose-red if absent.

Preparation of the reagent

1. Iodoplatinate
   1 ml. 5% platinic chloride and 5.3 ml. 5% sodium iodide diluted to 180 ml. with water.

2. Starch.
   1 gm. soluble or arrowroot starch rubbed to a smooth paste with cold water and the paste added to 200 ml. boiling water. Allow to cool and add 2 drops of toluene as preservative. Keep stoppered.

The sensitivity of the above test is 0.005 mgm. of mustard gas. It is reasonably specific; phosgene, diphosgene, chloropicrin, brombenzyl-cyanide, ethyl iodoacetate vapors give no reaction while the arsenical vesicants do not interfere unless present in exceptionally high concentrations, when they tend to decolorize the reagent (sulfur dioxide has a similar decolorizing action). Chlorine and nitrous fumes, of course, give a positive test, and the detection should be carried out by aspirating air through the contaminated sample, in order to eliminate interference from such gases.

Beta naphthol test

The suspected gas is passed through a freshly prepared solution of beta naphthol in aqueous-alcoholic alkali. If mustard gas is present the corresponding di-beta naphthyl ether (m.p. 133° C.) is slowly precipitated as a white turbidity (accelerated on warming).

$$S(CH_2CH_2Cl)_2 + 2C_{10}H_7ONa \longrightarrow S(CH_2CH_2O \cdot C_{10}H_7)_2 + 2NaCl$$

Preparation of the Reagent

1. 10% alcoholic solution of betanaphthol
2. Approx. N/10 sodium hydroxide.

Add 100 ml. of the alkali solution to 1 ml. of the naphthol solution. The mixture turns brown on keeping so that the two solutions should be mixed just before using.

The sensitivity of the above test is given as 0.01-0.06 mgm. of mustard gas.

Lewisite (M-1), chlorvinyldichlorarsine, $Cl\text{-}CH\ CHAsCl_2$

1. Lewisite is rapidly hydrolyzed by water with the production of hydrochloric acid and chlorvinylarsenious oxide. The hydrolyzed solution will therefore give the reactions for acid, chloride and arsenic.

2. When lewisite is decomposed by alkali, acetylene is formed which may be detected with cuprous chloride paper.

Pass the gas through 1 ml 15% NaOH. Acetylene can be recognized by suspending a piece of cuprous chloride paper above the alkali. A red stain on the test paper indicates that acetylene was formed and that lewisite was present. Sensitivity: 0.02-0.05 mgm/ml. solution.

PREPARATION OF CUPROUS CHLORIDE PAPER

1 gm. cupric sulfate (or preferably nitrate) dissolved in small quantity of water, add 4 ml.conc. ammonium hydroxide and 3 gms. hydroxylamine hydrochloride, shake until mixture is colorless. Make up to 50 ml. If the reagent is covered with mineral oil or a piece of copper wire is added it will retain its activity. Filter paper may be saturated in this solution and used at once as stated above.

Ethyldichlorarsine (ED), $C_2H_5AsCl_2$ and Methyldichlorarsine (MD) CH_3AsCl_2.

Hydrogen Sulfide Test

Aspirate the suspected gas through small amount of water. Add a few drops of hydrogen sulfide water; an opalescence or turbidity of the arsine sulfide is obtained if the amount of primary arsine exceeds 0.02-0.05 mgm/ml. solution. If the turbidity redissolves on addition of more hydrogen sulfide water, lewisite is present. Sensitivity: 0.02-0.05 mgm. primary arsine.

Mercurous Nitrate Test

This test is less sensitive than the hydrogen sulfide test but is of greater value for differentiating between lewisite and the other alkyl dichlorarsines. The test is based on the reaction of the arsines with a solution of mercurous nitrate acidified with nitric acid. With lewisite a white precipitate is obtained; with ethyl dichlorarsine a white precipitate slowly changing to grey (reduction to metallic mercury) and with methyl dichlorarsine an immediate grey precipitate is formed. Sensitivity: 1 mgm. methyl, ethyl or chlorvinyldichlorarsine.

Gutzeit Test for Arsenic

This test depends on the reaction of arsine with mercuric chloride or bromide paper to give a yellow-brown stain. This reaction is carried out in a small bottle where hydrogen is generated by means of zinc and hydrochloric acid in presence of the sample, the gases pass out through sand moistened with lead acetate to absorb any hydrogen sulfide which would interfere. The gases then pass across the mercuric chloride test paper. A yellow or yellow-brown stain indicates arsine. A blank should be run on the reagents by reacting zinc and HCl in the generator in the absence of the sample. The paper should show no stain. The details are as follows:

Use a 2 oz. wide mouth bottle as generator. The bottle is equipped with a one-hole rubber stopper carrying a glass tube 1 cm. in diameter and 6-7 cm. long, with one end narrowed down to facilitate its insertion in rubber stopper. Place a small wad of glass wool in the constricted bottom end of the tube and add 3.5 - 4 gm. 30 mesh clean sand. Moisten the sand with 10% lead acetate solution and remove the excess with light suction. Connect the top of this tube by means of a rubber stopper with a narrow glass tube about 3 mm. in internal diameter, and 10-12 cm. long and place in this a strip of mercuric bromide (or chloride-5% aqueous) paper. These strips are made by cutting filter paper (similar to Whatman No. 40) into strips about 2.5 mm. wide and about 12 cm. long. Soak the strips for 1 hour or longer in fresh 3-6% solution of mercuric bromide in 95% alcohol. Dry and use within two days. Store in well stoppered blackened tube, preferably containing P_2O_5, as papers are sensitive to light and moisture. To make a test for arsenic add 5 cc conc. HCl (arsenic free) and 2-4 gm granulated zinc (arsenic free) to the bottle, stopper and let stand for 2 minutes, if no darkening of test paper occurs the blank on the reagents is satisfactory. Insert the sample, stopper the bottle again and let stand. If arsenic is present in considerable amount in the sample the test paper will begin to change color after several minutes.

This method can be applied directly to the nose irritants, which are aerosols. The cotton filter used to collect the sample is extracted with alcohol and the alcohol extract used in the Gutzeit test. For the substances which are diffused in the air as vapors it is necessary that the sample be collected on silica gel. The silica gel with the absorbed gas is boiled for 1 hour with 10 ml H_2SO_4 and 1 ml HNO_3, cooled, 50 ml H_2O added and the sample evaporated to fumes. After cooling the sample is washed into a Gutzeit generator.

CHLORINE (Cl)

O-Tolidine Paper

O-tolidine (0.1 gm) is dissolved in 100 ml. 10% hydrochloric acid. Filter paper moistened with this solution gives a yellow-orange color in the presence of chlorine.

(2) Potassium Bromide-Fluorescein Paper

0.2 gm. fluorescein, 30 gm. of potassium bromide, 2 gm. potassium hydroxide and 2 gm. sodium carbonate are dissolved in 100 ml. water. Filter paper moistened with this solution and dried changes color from yellow to red in presence of chlorine.

Phosgene (CG) Carbonyl chloride, ClCOCl, and
Diphosgene, Trichlormethylchlorformate $ClCOOCCl_3$

(1) Dimethylaminobenzaldehyde - diphenylamine paper

5 gm. of the substituted benzaldehyde and 5 gm. diphenylamine are dissolved in 100 ml. alcohol. Filter paper is soaked in this reagent and then allowed to dry in a dark place. Test papers should be kept in closed container preferably filled with carbon dioxide and protected from the light. By exposing these papers, (originally white or pale straw yellow) to an atmosphere containing phosgene an orange yellow coloration is produced in a few seconds, the intensity of the color varying with the concentration of phosgene. This change of color is also observed in the presence of chlorine and hydrochloric acid.

It is possible to detect phosgene at a concentration of 4 mgm. per cu. meter of air. The British say 1 part phosgene is detectable per 1 million parts air. To remove traces of chlorine and hydrochloric acid is testing, draw the air first through a guard tube containing pumice impregnated with sodium thiosulfate before it comes in contact with the test paper.

(2) Nitrosodimethylaminophenol Paper

Two solutions are prepared in xylene:

(a) 0.1 gm. 1,3,6 nitrosodimethylaminophenol in 50 ml. xylene.
(b) 0.25 gm. m-diethyl aminophenol in 50 ml. xylene.

5 ml. solution "a" are mixed with 2 ml. solution "b" and strips of filter paper immersed in the mixture and allowed to dry. The paper should be dampened with 50% alcohol just before use as the dry paper does not give the test. In the presence of phosgene the color changes from white to green.

These papers are specific for phosgene and are more sensitive than the dimethyl amino benzaldehyde papers. Sensitivity is 0.8 mgm. per cu. meter of air.

The two solutions should not be kept mixed for more than 4 days.

(3) Aniline Reagent

By passing the suspected gas through a saturated solution of aniline diphenylurea is formed which precipitates. By saturating the test reagent with diphenylurea the reaction is made more sensitive.

3 gm. of aniline are dissolved in 100 ml. of water and the mixture saturated with diphenylurea and then filtered to remove excess. On passing air containing phosgene or diphosgene through this reagent a white turbidity of diphenylurea is obtained (mp. 236° C.). This reaction will detect 0.2 mgm of phosgene and can be applied quantitatively by weighing the precipitate after washing and then drying at 70° C. By passing 5 liters of gas mixture (velocity 200 ml./minute) it is possible to detect 40 mgm phosgene per cu. meter of air.

CHLOROPICRIN (PS), CCl_3NO_2

The detection of chloropicrin is most simply carried out by direct sensory perception. None of the chemical methods are as sensitive as odor perception.

(1) Nitrite Test

This reaction depends on the formation of nitrite when chloropicrin is hydrolyzed with sodium ethylate.

$$C\,Cl_3\,NO_2 + 4C_2H_5ONa \longrightarrow C(OC_2H_5)_4 + 3NaCl + NaNO_2$$

The presence of nitrite is demonstrated by the Griess-Illosvay reagent (sulfanilic acid and naphthylamine).

Dissolve a drop of the poison gas freed from nitrous fumes in or aspirate the gas into 5 cc. of alcohol. Add a small piece of 8% sodium amalgam. After a few minutes decant the solution from the mercury. Acidify with acetic acid adding the acid drop by drop and then add 1-2 ml. of the Griess sulfanilic acid and naphthylamine reagent. After 10 minutes heat on the water bath. If much nitrous acid is present the red coloration will form in the cold.

Reagents

(a) 8% Sodium Amalgam

Weigh out 8 gm. of sodium metal which is clean. Place 92 gm. clean dry mercury in a mortar. Cut the sodium metal in small pieces, and after cutting each small piece dry quickly with filter paper and use a stirring rod with a sharp point on which to impale the sodium and plunge under the surface of the mercury. Goggles should be worn and face should be averted when placing the sodium in the mercury. Hold each piece under the surface until evidence of reaction occurs. The amalgam will become stiff after most of the sodium is added and the sodium should be moved around under the surface to stir the amalgam. When all the sodium is added and while still hot pour the amalgam onto a piece of asbestos board. When cool enough to handle break up the layer of amalgam and place in a tightly stoppered bottle.

Griess-Illosvay Reagents

(a) Dissolve 1 gram of sulfanilic acid in hot water; cool and dilute to 100 ml.

(b) Boil 0.5 gm. of alpha-naphthylamine hydrochloride with 100 ml. of water kept at constant volume for 10 minutes. Decolorize with activated charcoal if necessary.

or

(a) 1 gm. sulfanilic acid is dissolved in hot water containing 14.7 ml. glacial acetic acid and made up to 300 ml. with water.

(b) 0.2 gm. alpha-naphthylamine is dissolved in water containing 14.7 ml. glacial acetic acid and made up to 350 ml. with water.

For the test 1 ml. of each solution is used. The reagent is very sensitive and a blank test should be run simultaneously on the reagents. Sensitivity -- 6 mgm per cu. meter of air.

The presence of nitrite is practically specific as an indication of the presence of chloropicrin for other chemical agents containing nitro groups are seldom used. It should be mentioned, however, that the development of vapor phase nitration of aliphatic hydrocarbons has made simple aliphatic nitro compounds easily available. Chloropicrin can already be made easily by the use of these compounds. Nitro compounds other than chloropicrin, being easily available, may find use in the present war.

Dimethylaniline Test

Expose the test paper which is white in color to the atmosphere to be tested or if the concentration is low wave gently in the suspected atmosphere. This paper changes from white to yellow or maroon in the presence of chloropicrin.

Preparation of dimethylaniline test papers

Soak strips of filter paper in a 5-10% solution of dimethylaniline in benzene.

Chlorine, bromine and nitrous gases also give a color with this reagent but of a different shade. The color change takes place only with strong concentrations of chloropicrin and preferably in contact with the liquid gas.

Carbylamine, thymol and sodium sulfide tests also are available for detection of chloropicrin and the combustion method is preferable for quantitative determination.

DETECTION OF NOSE IRRITANTS

The main irritants considered here, diphenyl chlorarsine, diphenylcyanarsine and diphenylamine chlorarsine (Adamsite) are all used in the form of particulate clouds which means they will not be absorbed by passing through reagents. It is necessary to use filters to catch the small particles, and then to test the filter for arsenic or if a reasonable amount of particulate matter has been collected to extract the filter with hot alcohol, evaporate the extract on a water bath and examine the residue for the elements, m.p. etc., or to use the alcoholic extract to test for the various nose irritants. Either the residue or the alcoholic extract may be used for detecting the presence of arsenic by the Gutzeit method. In the case of particulate clouds the presence of one of the arsenicals will be indicated by the presence of arsenic in the deposit on the filter.

To determine whether or not the smoke consists of chloracetophenone, a lachrymator used in the form of a non-persistent particulate cloud, a portion of the extract is treated with iodine-starch solution and sodium bicarbonate. If the arsenical smokes are present the blue color will disappear due to the reduction of free iodine to iodide by the trivalent arsenic of the arsenicals which is oxidized to the valence of five.

Diphenylchlorarsine (DA) $(C_6H_5)_2\ AsCl$

(1) To an alcoholic extract of the deposit on the filter is added an equal volume of 95% alcohol saturated with hydrogen sulfide and the mixture is cooled in ice water. Diphenylarsenious sulfide is precipitated (m.p. 67° C.).

$$2(C_6H_5)_2\ AsCl + H_2S \longrightarrow [(C_6H_5)_2\ As]_2\ S + 2HCl$$

(2) To 5 cc of an alcoholic extract of the filter add 4 drops of 5% alcoholic potassium hydroxide and warm. Diphenylarsenious oxide (m.p. 92° C) is precipitated.

$$2(C_6H_5)_2\ As\text{-}Cl + 2KOH \longrightarrow 2KCl + [(C_6H_5)_2As]_2O$$

Diphenylcyanarsine (CDA) $(C_6H_5)_2$ AsCN

(1) Hydrogen cyanide test

Alcoholic extract (5 ml) is hydrolyzed with 5% alcoholic potassium hydroxide. After cooling, acidify the solution with dilute sulfuric acid. Have a piece of benzidine-copper acetate paper suspended in the vapor while warming the tube. A blue color appears in the presence of cyanide.

Reagent

Benzidine Copper Acetate Paper

(a) 2-3 gm. pure benzidine acetate heated to 80° C. in 100 ml. distilled water for 10-15 with constant shaking. When cold filter by suction; the filtrate contains approximately 1% benzidine acetate.

(b) 3 gm. copper acetate $Cu(C_2H_3O_2)_2$ H_2O are dissolved in 100 ml. distilled water. Immediately before use 25 ml. of the benzidine acetate solution and 2 ml. of the copper acetate are mixed and stirred well. The test papers are dipped in the solution, allowed to drain and then dried until just moist. The mixed solution does not keep nor do the papers; they must be used immediately after preparation.

(2) A more specific test for cyanides is the Prussian Blue test. After hydrolyzing add a crystal of ferrous sulfate and heat for a minute. Then acidify with hydrochloric acid. A Prussian Blue color indicates cyanide.

Diphenylamine chlorarsine (DM) (Adamsite) $HN(C_6H_4)_2$ AsCl

(1) The alcoholic extract is evaporated to dryness by gentle heat. A drop of concentrated sulfuric acid is added to the residue. An intense red color, changing to blue green on addition of a drop of nitric acid indicates diphenylamine, an impurity usually found in industrial adamsite.

(2) The alcoholic extract is evaporated to dryness. 5 ml. of a misture of equal parts of 10% silver nitrate solution and glacial acetic acid are added. An intense yellow color is produced on standing for 10 minutes in the presence of Adamsite. If diphenylamine is present a dirty green color forms which gradually changes to black.

LACHRYMATORS

Brom-acetone Br. CH_2COCH_3

(1) Sodium Nitroprusside test

The vapor is passed through 0.5 N. alcoholic potassium hydroxide, which decomposes the bromacetone to potassium bromide and hydroxy acetone. This ketone is identified by the addition of a few drops of a 1% sodium

nitroprusside solution which forms a red color with the acetone derivative. The color of the acetone derivative is intensified by addition of acetic acid.

(2) Indigo Test

The gas is passed into sodium hydroxide solution and a few drops of an alcoholic solution of o-nitrobenzaldehyde added. The latter reacts with the acetone derivative to form indigo which is recognized by its purple color. This test is not as sensitive as the nitroprusside test.

An alcoholic extract may be used for the above tests.

Ethyl Iodoacetate $ICH_2COOC_2H_5$

(1) Glycollic Acid Test

The gas is aspirated into 0.5 N. alcoholic potassium hydroxide. The solution is acidified and a portion is tested for iodide with silver nitrate giving a yellow precipitate of silver iodide if the gas is present. To the remainder of the solution is added a crystal of guiacol and a few drops of concentrated sulfuric acid. A violet color indicates the presence of glycollic acid formed by hydrolysis of ethyl iodoacetate:

$$ICH_2COO\ C_2H_5 + 2KOH \longrightarrow KI + \underset{\text{Glycollic acid (K salt)}}{HOCH_2COOK} + C_2H_5OH$$

An alcoholic extract of the gas may be used for this test.

Chloroacetophenone (CN) ($C_6H_5COCH_2Cl$)

Chloroacetophenone has adequate warning properties in very low concentrations and this irritant action may be used as a means of detection. Since it is used in the form of a non-persistent particulate cloud it is doubtful whether any sample will be obtained.

An alcoholic extract should be used whenever possible.

(1) Benzoic acid test

Treat 1 ml. of the alcoholic extract with 5 ml hot alkaline permanganate solution (6 gm$KMnO_4$ and 1 gm. NaOH dissolved in water and diluted to 100 ml.). Acidify with sulfuric acid and extract with ether. The residue upon evaporation of the ether is dissolved in water and tested with a drop of ferric chloride solution. A buff colored precipitate indicates benzoic acid. (Benzyl bromide gives similar result).

(2) Hydrogen Sulfide Test

If the alcoholic extract contains sufficient gas the following test may be applied. Add 20% aqueous-alcoholic (50:50) sodium sulfide and warm, if necessary, to effect reaction; cool and dilute with water.

$$2\ C_6H_5COCH_2Cl + Na_2S \longrightarrow (C_6H_5 - CO\text{-}CH_2)_2\ S + 2NaCl$$

The sulfide precipitate, diphenacyl sulfide has a m.p. of 77° C.

<u>Benzyl Bromide</u> $C_6H_5CH_2Br$

The alkaline permanganate test applied to benzyl bromide gives the same result as for chloracetophenone. However, upon treatment of this gas or its alcoholic extract with alcoholic silver acetate, silver bromide and not silver chloride is precipitated.

<u>Xylyl Bromide</u>

The principal method for distinguishing Xylyl bromide depends on the invariable presence of the ortho isomers which upon oxidation with alkaline permanganate yield phthalic acid.

This can then be treated to form fluoroscein which is identified by its green fluorescent solution.

Treat 1 ml of the alcoholic extract with 5 ml of hot alkaline permanganate solution. Acidify with sulfuric acid and extract the phthalic acid with ether. Evaporate the ether extract to dryness. Add 5 ml concentrated sulfuric acid and a small amount (.025 gm) of resorcinol. Heat in a paraffin bath or very carefully over free flame (at 160° - 170° C) for about 10 minutes. Cool and pour into water. Add sodium hydroxide solution to make alkaline. Green fluorescence appears if xylyl bromide was present in the original extract.

<u>Brombenzylcyanide</u> (CA) C_6H_5 CH CNBr

This compound is such a powerful lachrymator and has such adequate warning properties that these in themselves serve as a means of detection.

(1) By use of an alcoholic extract of the sample of aspirating the gas through 10% silver nitrate solution and then boiling, a reduction of the silver nitrate occurs to metallic silver. The brombenzyl cyanide is converted to benzaldehyde which can be recognized by its characteristic odor.

(2) An alcohol extract of the gas is treated with 0.5 N. alcoholic potash. On boiling the mixture ammonia is evolved. If the solution is cooled and acidified, a yellow precipitate of diphenyl maleic anhydride which melts at 156° C is obtained.

$$C_6H_5 - \underset{\substack{|\\ Br}}{\overset{\substack{H\\ |}}{C}} - CN + KOH \longrightarrow C_6H_5 - \underset{\substack{|\\ CN}}{\overset{\substack{H\\ |}}{C}} - \underset{\substack{|\\ CN}}{\overset{\substack{H\\ |}}{C}} - C_6H_5$$

$$C_6H_5 - \underset{\substack{|\\ CN}}{\overset{\substack{H\\ |}}{C}} - \underset{\substack{|\\ CN}}{\overset{\substack{H\\ |}}{C}} - C_6H_5 + H_2O \xrightarrow{\text{boiling}} \begin{array}{l} C_6H_5 - C - \overset{O}{\overset{\|}{C}} \diagdown \\ \qquad\quad \| \qquad\qquad O + 2NH_3 \\ C_6H_5 - C - \underset{\|}{\underset{O}{C}} \diagup \end{array}$$

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Monochlormethyl Chlorformate $ClCOOCH_2Cl$

The gas is aspirated through water where it is hydrolyzed to formaldehyde. On addition of a drop of a 1% phenol solution and then a layer of conc. sulfuric acid carefully run in; a red zone is formed at the interface between the sulfuric acid and water layers. This reaction is not given by diphosgene (trichlormethylchloroformate) or by dichlormethyl chloroformate.

Hydrocyanic acid, hydrogen cyanide, HCN

(1) Benzidine and copper acetate test

The benzidine and copper acetate test is one of the most sensitive and widely used tests for the detection of hydrogen cyanide in air. It depends upon the production of a blue color with moist freshly prepared benzidine and copper acetate test paper (within 3 to 30 seconds) in the presence of an atmosphere containing hydrogen cyanide.

Procedure

Place a freshly prepared test paper into a holder and attach to a hand exhausting pump which has a barrel capacity of approximately 125 ml. Make a preliminary test of the atmosphere by making eight slow and steady strokes with the pump. Remove the paper and compare with the stains on standard charts.* In this way an estimate may be made of any concentration between 1 part in 10,000 and 1 part in 20,000 of air by volume. The latter is the maximum concentration that can be inhaled for 1 hour without serious disburbance. If the stain indicates a concentration greater than 1 part in 20,000 a fresh paper is placed in the holder and further tests are made with 1, 2, 3 or 5 strokes of the pump; or if a concentration of less than 1 in 100,000 is indicated a rough estimate of the concentration may be obtained by repeating the test with a greater number of strokes. Comparison of the stains should be made in diffused daylight or with the aid of a daylight lamp.

Reagents

(1) Benzidine acetate solution. Heat two to three grams of pure benzidine acetate in 100 ml. of water for 10 to 15 minutes at 80° C. with constant stirring. When cold filter the mixture by suction. The filtrate will contain about one percent benzidine acetate.

(2) Copper acetate solution - Dissolve three grams of acetate, $Cu(C_2H_3O_2)_2\ H_2O$ in 100 ml. of water.

Immediately before the test is made mix 25 ml. of the benzidine acetate solutions with 2 ml. of copper acetate solution and stir well. The mixed reagent will not keep more than 15 minutes.

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*Dept. of Sci. Ind. Research Brit. Leaflet No. 2 (1938)

The test papers may be prepared from extra thick white filter paper cut into strips 2 inches wide. Immerse them in the mixed reagent for 1 minute, drain and allow to dry in a warm atmosphere. Cut off one inch at the top and bottom of the strip and discard. Cut the remainder of the strip into 3 inch lengths. The papers must be used immediatedly.

(2) The Methyl Orange-Mercuric Chloride Test.*

This test which is not as sensitive as the first mentioned depends on the change in color produced in a methyl orange-mercuric chloride paper by hydrocyanic acid. The color changes from orange to pink. These papers may be prepared in advance at a convenient place and under conditions of 70 to 75 per cent relative humidity will keep in a tightly stoppered bottle for as long as 30 days.

Procedure

The test is made by carrying the paper in a small vial to the place to be tested and exposing the paper to the atmosphere for two minutes. A definite pink color at the end of this time indicates a dangerous concentration of hydrogen cyanide gas in the air unless the humidity is great enough to accelerate the reaction. The test can also be made by clipping the paper to a line carrying a small lead weight or casting plug, casting the paper with a casting rod and reel into the area to be tested and withdrawing the paper for examination after two minutes. Chlorine, hydrochloric acid or any compound hydrolyzing to give acid in a moist atmosphere will affect the color of the methyl orange-mercuric chloride test papers. The following table shows the relationship of the hydrogen cyanide concentration, color of test paper and time of test.

Methyl Orange-Mercuric Chloride Test

Grams HCN per 1000 cubic feet	Duration of Test in Minutes				
	0.5	1	1.5	2	3
6.7	slight pink at edge	faint pink	definite pink	red	red
3.35*	no change	slight pink at edge	faint pink	definite pink	red
1.68	no change	no change	bright orange	faint pink	faint pink

*Sherrard G. C., U. S. Public Health Service Reprint No. 1224 (1928)

*This was the minimum lethal dose for exposure of white rats for 12 hours in a gas tight compartment.

Grams HCN per 1000 cubic feet	Duration of Test in Minutes				
	0.5	1	1.5	2	3
0.84	no change	no change	no change	slight pink	very faint pink
0.42	no change	no change	no change	no change	no change

Reagents

(1) Mercuric chloride solution: - Dissolve 5 grams of mercuric chloride in 250 ml. of distilled water.

(2) Methyl orange solution: - Dissolve 0.60 g. of methyl orange in 250 ml. of distilled water. Mix 10 ml. of mercuric chloride solution with 5 ml. of methyl orange solution and add 1 ml. of glycerine.

Sheets of filter paper are immersed in this solution and hung up to dry in air which is free from any trace of acid. When dry cut the filter paper into strips $\frac{1}{4}$ inch wide and preserve them in glass tubes protected from the light.

(3) Additional methods which can be used for quantitative estimation of hydrocyanic acid in the laboratory include the thiocyanate method and the well known Liebig silver nitrate method. For a description of these procedures see M.B. Jacobs', "Analytical Chemistry of Industrial Poisons, Hazards and Solvents", Interscience Publishers, 1941.

Table 3

IDENTIFICATION OF COMMON CHEMICAL AGENTS BY ODOR AND OTHER IMMEDIATE EFFECTS

Class	Agent	Symbol	Odor: Character	Odor: Threshold mg. per cu. meter	Other immediate effects: Nature	Other immediate effects: Threshold of action mg. per cu. meter
Vesicants	Mustard	HS	Garlic, horseradish	0.3	None	--
	Lewisite	M-1	Geraniums	1	Nose and throat irritation	2
	Ethyl-dichlorarsine	ED	Fruity, pungent irritant	0.8	Nose and eye irritation	1.5
Lung Injurant	Phosgene	CG	Musty hay, cut corn, silage	5-10	Thin white cloud produced coughing, tightness in chest	10-15
	Chlorpicrin	PS	Sweetish, fly-paper, like licorice	8	Lacrimation, vomiting	15-20
Lacrimators	Brombenzyl-cyanide	CA	Sour fruit. (Irritates before odor is noticed)	0.2	Lacrimation, nose irritation	.2
	Chlor-acetephenone	CN	Locust or apple blossoms		Lacrimation Skin irritation	.3 2
	CN Solution	CNS	Sweetish		" "	
Irritant Smokes	Adamsite	DM	Odor from burning smokeless powder	--	Canary yellow smoke, headache, vomiting	0.1
	Diphenyl-chlorarsine	DA	Aromatic, irritant	0.3	Sneezing, headache, vomiting	0.1
Screening Smokes	HC Mixture	HC	Smoky, camphor like	--	Dense smoke, slight suffocating feeling	--
	SO_3 in $HClSO_3$	FS	Acid (strong)	--	Dense smoke, eye irritation, prickly sensation on skin	--
	Titanium tetrachloride	FM	Acid(mild)	--	Slight eye irritation, dense smoke	--
Sys-temic Poison	Hydro cyanic acid	--	Bitter almonds	1.0	Headache, dizziness, collapse	20
	Carbon monoxide	--	None	--	Headache, collapse	--

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TABLE 4

CHEMICAL METHODS OF IDENTIFICATION

Name of Gas	Symbol (CWS)	Reagent or Test	Condition of Unknown	Nature of Positive Result	Interfering Substances	Sensitivity of Test
Mustard Gas	HS	Schroter's Gold Chloride	Gas-Aspirated through reagent	Yellow colloidal turbidity to yellow-red oil droplets	Specific	10 mgm./cu. m of air
			Gas-aspirated thru paper treated with $AuCl_3$	Reddish-brown stain		
			Gas-aspirated thru silica gel treated with $AuCl_3$	Yellow ring	Specific	12 mgm./cu. m of air
		Iodoplatinate	Gas	Iodine librated	Chlorine or nitrous fumes	0.005 mgm. ga
		Yablich's Selenious Acid	Gas	Yellow or reddish-orange suspension of selenium	All arsines and CO	5 mgm./cu. m. of air
		Beta Naphthol	Gas	White turbidity		0.01 - 0.06 m
		Grignard's Potassium Iodide	Gas	Yellow colloidal ppte. of diiodo ethyl sulfide	High conc. (4%) of aliphatic arsines & phenylcarbylamines	100 mgm./cu. of air or 0.0 mgm./ml. sol.
Lewisite	M-1	Acetylene Test	Liquid is preferable	Acetylene produced on reaction with 15% NaOH	Specific	0.02-0.05 mgm per ml. soluti or high conc. of gas in air
Ethyl and Methyl Dichlorarsine	ED and MD	Gutzeit Test	Gas or liquid	Brown stain on $HgCl_2$ paper	Any arsenical	
		Mercurous Nitrate	Gas	White ppte. turning to grey within few hrs. = Lewisite (M-1). White ppte. turning to grey in few seconds = C_2H_5AsCl (ED) Immediate grey ppte. = CH_3AsCl_2 (MD)		1 mg. of MD ED M-1
		Hydrogen sulfide water	Gas	Turbidity = primary alkyl dichlorarsine (M-1, ED, MD). If soluble in excess = M-1.		0.02 - 0.05 mgm. of gas

TABLE 4 (Continued)

CHEMICAL METHODS OF IDENTIFICATION

of Gas	Symbol (CWS)	Reagent or Test	Condition of Unknown	Nature of Positive Result	Interfering Substances	Sensitivity of Test
gene	CG	Dimethylamino benzaldehyde-diphenylamine test paper	Gas	Yellow or orange color	HCl, Cl_2, $ClSO_3H$ $TiCl_4$	4 mgm./cu. m. of air
		1, 3, 6 nitrose dimethylamino phenol-m.diethyl amino phenol test paper	Gas	Green color	Specific	0.8 mgm./cu. m. of air
		Aniline	Gas	White turbidity of diphenylurea	Specific	40 mgm./ cu. m. of air
or- rin	PS	Nitrite test	Gas	Nitrite present after hydrolysis	Specific	6 mgm./ cu. m. of air
		Dimethylaniline paper	Gas	Yellow or maroon color	Cl_2, Br_2 and nitrous fumes, but give different color	
raceto- hone	CN	Alkaline $KMnO_4$	Alcohol extract	Benzoic acid formed	Benzyl bromide	
		Sodium sulfide	Alcohol extract	Diphenacyl sulfide formed		
nbenzyl- nide	CA	Silver Nitrate	Liquid or extract	Ag ppted.; benzaldehyde formed		
		Alcoholic Potash	" " "	Diphenylmaleic anhydride formed		

METHODS FOR DETECTION OF CHEMICAL WARFARE AGENTS IN WATER AND TREATMENT OF CONTAMINATED WATER SUPPLIES*

By
C. C. Ruchhoft and Stuart Schott

The possibility of contamination of our water supplies by war gases is open to the same arguments, pro and con, as the possibility of gassing civilian populations. These actions probably would not be attempted, except against untrained civilians. Heretofore, the only poisoning of water supplies by poison gas was accidental.

Protection of our water supplies in reservoirs depends on the increasing vigilance of our waterworks personnel. Systems for guarding our waterworks against trespassers or possible saboteurs have, in most cases, already been put into operation. In a similar manner we must be on the alert to protect against any poisoning by war gases and to have a plan of action, should contamination occur.

It might be said that the results obtained by an enemy in poisoning our water supply probably would not equal the effect caused by the same weight of high explosive or incendiary bombs, but this is pure speculation. We must consider the possibility of accidental or deliberate contamination during a gas attack on a city, especially if the element of surprise was present. It should be emphasized that the success or failure of such an attack depends as much on our advance preparations as on the skill of the enemy.

The chemical warfare agents may be divided into a number of groups, according to their effectiveness in producing toxic contamination of water supplies. Such a classification of the common important agents has been presented by Leitch.[1] A slight modification of this classification is given in Table 1. Group 1 in this table includes Thermit, Crude Oil, FS Mixture, FM and Carbon Monoxide, all of which would not produce a toxic water although the taste and odor might be accentuated to produce an unpleasant tasting water which might not be potable.

Group 2 includes the arsenical irritant smokes such as Adamsite and Diphenylchlorarsine. These substances are insoluble and stable in water. Consequently, if the sources of supply were contaminated with these agents, the standard water purification processes, including coagulation, settling, filtration and chlorination would remove them and produce a safe potable water.

Group 3 includes phosgene which might be present in considerable concentration and would still result in a non-toxic water. Group 4 contains the vesicants and chloropicrin, the presence of which would

*From the National Institute of Health, Div. of Public Health Methods, Cincinnati Laboratory.

cause the greatest difficulty in water supplies. Brombenzyl cyanide and chloracetophenone are put into Group 5 because little data are available on their effects in water supplies. More information on the reactions and effects of these agents in water is needed. Compounds other than chemical warfare agents which are likely to be used for deliberate contamination of water supplies are listed in Group 6.

To show the basis for the above grouping of the chemical warfare agents, the solubility, behavior and products of hydrolysis of the more important agents are shown in Table 6. The treatment ordinarily required for water that has been contaminated by these agents is shown in the right hand column.

Mustard gas, which is likely to give trouble in water supplies is soluble to the extent of 800 p.p.m. at 20° C. When discharged into water the mustard gas is distributed into a surface film and a water soluble fraction and any excess present settles to the bottom. The undissolved mustard may remain unchanged for several weeks at the bottom of the water. The soluble fraction is hydrolyzed according to the following reaction:

$$(ClCH_2CH_2)_2S + 2HOH \longrightarrow 2HCl + \underset{\text{Thiodiglycol}}{(CH_2OHCH_2)_2S}$$

The thiodiglycol formed is soluble in water and is non-toxic. The rate of hydrolysis depends upon the quantity of gas present, the temperature and the alkalinity of the water. Boiling destroys mustard in 15 to 30 minutes but 2 or 3 days are required if storage at ordinary temperature is used.

The armed services of our country consider water containing 500 p.p.m. or more of mustard as impossible to treat for drinking purposes. With less than 500 p.p.m. the water may be treated if the following procedures can be employed. Treatment with unusually large doses of activated carbon followed by coagulation with the common coagulants and settling. The settled water is then filtered and chlorinated beyond the break-point. However, if the filtered water has a 5-minute chlorine demand of more than 5 p.p.m. the water is still unsatisfactory and must be retreated. For small doses of mustard (50 p.p.m. or less) the hydrolysis reaction will be sufficiently complete after one hour to permit use of the water from intermediate reservoir levels. Where other sources of water are available finished water reservoirs should be pumped to waste if contaminated with mustard gas to any extent.

Water contamination by lewisite, ethyl dichlorarsine of methyldichlorarsine would also give trouble. Lewisite is the least soluble of these gases but all of them are rapidly hydrolyzed. The chlorvinyl, ethyl and methyl arsenious oxide hydrolysis products are all sufficiently soluble to be dangerous in a water supply. These soluble arsenious oxides cannot be removed by ordinary water purification processes. Consequently, the extent of the contamination should be determined by complete sampling and careful analytical procedures for arsenicals. If the arsenic content does not exceed 1 to 5 p.p.m. the water would be

safe to use for periods varying from one day for the higher concentration to one week for the lower concentration. If larger quantities of arsenic are found, or if other non-contaminated supplies are available, the water should be pumped to waste. These suggested limits for arsenic under emergency conditions are very much higher than the arsenic limit in the latest Public Health Service Drinking Water Standard[2] (Arsenic not to exceed 0.1 p.p.m.). The Public Health Service limit applies to waters which may be used continuously, while the limits suggested here apply under emergency conditions to supplies that are to be used only for periods of one week or less. Methods for detection of arsenic are given later in this memorandum.

The last of the gases in group 4 which is likely to give trouble in water is chloropicrin. Chloropicrin is slowly soluble to the extent of 1700 p.p.m. is very stable and is not hydrolyzed by water. If a water supply was heavily contaminated with it most of the chloropicrin would settle to the bottom of the reservoir after which it would slowly go into solution. Ordinary water treatment processes are ineffective in its removal. Once the chloropicrin is dissolved in the water excessive doses of activated carbon could not be relied upon to remove it. It can best be detected by its characteristic sweetish odor in concentrations down to as little as 5 p.p.m. in water.

Its odor and taste are easily noticeable at 10 to 20 p.p.m. A concentration of 40 p.p.m. gives a burning sensation to the tongue within a few seconds, and might be considered beyond the limit of potability. A water containing 80 p.p.m. or more will produce lacrimation. The odor and taste indications of chloropicrin in a water can be confirmed by the nitrite test after boiling a small sample of the water with alcoholic potassium iodide to decompose the gas. It is suggested that 20 p.p.m. be taken as the upper limit of potability for chloropicrin. Waters containing quantities of 100 p.p.m. or more might be made potable by aeration for several hours or by storage in open reservoirs for 1 or 2 days. Additional experimental work is needed to determine more exactly the upper limit of safety for chloropicrin and possible treatment procedures for its removal.

The lung injurant, phosgene, is soluble to the extent of 1000 p.p.m. in water and is rapidly hydrolyzed to HCl and CO_2. Consequently, no toxicity is produced with phosgene contamination after hydrolysis has been completed. If the pH of the water is lowered to the extent that it is unpleasant to the taste this can be easily adjusted with lime.

The lacrimators, brombenzyl cyanide and chloracetophenone have been put in Group 5, for which additional information is required. These agents are considered insoluble and stable by all authorities. Consequently, they would be largely removed from raw waters by complete water purification processes. The extent to which they could be permitted in treated waters remains to be determined.

The irritant smokes including adamsite, diphenylchlorarsine and diphenylcyanarsine are either insoluble and stable or very slightly soluble and slowly hydrolyzed. These arsenical agents would, therefore,

produce a turbid water which could be purified by the complete water treatment processes. If contamination with these agents is suspected in clear water reservoirs, samples of the water should be examined for chlorine demand and arsenic, and the limits for arsenic already suggested for lewisite should not be exceeded. If additional water supplies are easily available, contaminated reservoirs should be pumped to waste even if they contain arsenic in concentrations within the above limits.

The screening smokes do not produce toxic products and need give little concern. Although adjustment of the pH may be necessary with heavy contamination of these agents, no other treatment will be required. While titanium hydroxide will be formed by the hydrolysis of titanium tetrachloride (FM) there is no evidence that this material is toxic. Titanium salts have, in fact, been suggested for use as coagulants in water purification.

The possibility of the introduction of cyanide by saboteurs or by hydrogen cyanide bombs, should not be overlooked. Simple tests for cyanide in water are available and should be made if cyanide contamination is suspected. Finished waters should be pumped to waste if cyanide is found. In raw waters the cyanide can be removed by treatment of the neutral or alkaline water with ferrous and ferric salts, followed by the standard water purification processes. This treatment would precipitate the cyanide as Prussian blue, most of which would then be removed by coagulation and filtration. As long as an excess of iron salts were used any blue color coming through the filter would be non-toxic.

An examination of Table 6 indicates that all of the troublesome chemical warfare agents with the exception of chlorpicrin hydrolyze with the production of acid; most of them contain arsenic and all of them increase the organic constituents of the water which would increase its oxygen consumed and chlorine demand values. Procedures to determine changes in the following criteria may be employed to detect contamination: (1) Odor and appearance, including turbidity, (2) pH, (3) Alkalinity, (4) Chloride content, (5) The oxygen consumed value, (6) The chlorine demand, (7) Presence of arsenic.

In devising any plan of action, it should be remembered that scientific personnel may not be on hand at all waterworks and the plan of detection should be arranged so that the tests will be as simple as possible to enable persons with the minimum of training to carry them out. The above simple criteria will probably suffice to indicate to an alert observer whether or not a gas warfare contaminant is present. The interpretation of the tests will be easier if a complete record of these criteria is kept from day to day. Most of these methods are capable of giving rapid results and are, therefore, as important as tests for any specific material.

In cases of attack with the vesicant gases, the same precautions must be observed by the waterworks personnel as by any other person in an area gassed with persistent vesicants. If the banks or the walls of the reservoir have been sprayed with these gases, protective clothing and gas masks will have to be worn even to sample the area to avoid injuries. Unless this protection is available the work of detection should be left to the Gas Officer. The detection of war gases and decontamination of any areas in the waterworks property which may be affected should be one of the first, if not the first job to be undertaken after a gas attack. Following this or simultaneously, if possible, the rapid tests for contamination of the water should be made to determine the extent of contamination, so that an immediate decision can be reached regarding the cutting off of the flow of water from a finished water reservoir or the initiation of emergency purification procedures.

Although most of the rapid tests given above are familiar to waterworks men, a short discussion of their applicability here may be helpful to some.

(1) Odor and appearance can be used to detect and identify some of the gases in contaminated water. The odor of mustard (HS) and lewisite (M-1) can be detected in many waters contaminated with 500 p.p.m. or more of these gases. In concentrations of 100 p.p.m. these gases cannot be detected. As already stated, chlorpicrin can be detected in concentrations as low as 5 p.p.m. by odor. Most of the war gases are heavier than water and if dropped into a reservoir will sink to the bottom, but may leave a thin film on the surface of the water or they may give an insoluble hydrolysis product which may be detected. The white chlorovinylarsenious oxide is formed immediately upon contact of

lewisite with water and rapidly settles to the bottom. Crude mustard looks like dirty crank case oil and this gas leaves a surface film which may remain for 24-48 hours. Solid particles on the water surface may be chloracetophenone (CN) or one of the irritant smokes (DM, DA, CDA). These gases are considered stable and insoluble and may be detected by increases in the turbidity.

(2) pH. An unusual lowering of the pH will indicate an acid hydrolysis product. Most waterworks laboratories are equipped with some apparatus to make these determinations which may be electromatric or colorimetric. The S.D.C. colorimetric pH kit, as an example, is portable and simple to use. Its use may be taught to one with little training in a short time. Among the gases which lower the pH by hydrolysis with the formation of a halogen acid are: mustard, lewisite, phosgene, diphosgene, ethyl dichlorarsine, methyl dichlorarsine, diphenylchlorarsine and possibly brombenzyl cyanide.

(3) Alkalinity. The alkalinity of the water is also lowered by hydrolysis of the above gases. This determination should be made by titrating 50 or 100 ml. of the sample with .02N standard sulfuric acid using methyl orange as an indicator(3). The effect of mustard and lewisite on the pH and alkalinity of Cincinnati tap water is illustrated in the following table:

Approximate Concentration of Gas in Tap Water p.p.m.	Mustard (HS)*			Lewisite (M-1)		
	pH	Alkalinity p.p.m.	Acidity p.p.m.	pH	Alkalinity p.p.m.	Acidity p.p.m.
0	7.6	38	--	7.8	38	--
10	7.2	34	--	7.3	34	--
50	5.5	7	--	6.2	15	--
100	3.4	--	21	3.5	--	10
500	2.4	--	256	2.8	--	200

(4) Chloride content. An increase in the chloride content may be detected by titrating the sample with standard silver nitrate solution using potassium chromate as an indicator(4), or by precipitating

(*) The mustard was allowed to react for one hour with frequent shaking before the tests were made. The water temperature was 27°C.

the chloride as the silver salt and completing the determination gravimetrically. An example of the chloride increase found by volumetric titration when Cincinnati tap water was contaminated with mustard and lewisite is given below:

Approx. Quantity of Gas Added p.p.m.	Mustard (HS)*		Lewisite (M-1)	
	p.p.m. Chloride		p.p.m. Chloride	
	Found	Theoretical	Found	Theoretical
0	18	18	18	18
10	25	22	23	21.4
50	45	40.3	35	35.1
100	67	62.7	49	52.2
500	254	241	168	189

(*) The mustard gas was allowed to react with the water for 24 hours before the chloride was determined.

(5). The oxygen consumed value is a chemical measure of the organic matter present in the water. It depends upon the oxidation of organic matter by a definite amount of standard potassium permanganate solution when heated with a sample of water in a boiling water bath for 30 minutes. The permanganate remaining after digestion is determined with standard ammonium oxalate solution and the permanganate absorbed is a measure of the oxygen consumed. As war gases are organic compounds they will be oxidized in the course of the oxygen consumed determination, leading to an increase of the oxygen consumed value above the normal value for the water. Other oxidizing agents such as potassium dichromate have been used for determining oxygen consumed, and dichromate possesses a slight advantage in oxidizing the organic matter more completely. It is suggested, however, that the permanganate procedure as given in Standard Methods[5] be followed for this work. Although the oxygen consumbed value is non-specific it would be advisable to set a standard which should not be exceeded for potable waters. As the oxygen consumed values of most drinking waters are 1 p.p.m. or less, higher values will indicate organic contamination. An increase in the oxygen consumed value of 2 or 3 parts should be looked on with suspicion. If the O.C. is increased 5 p.p.m. or more, the water should not be used unless it has been proven that this increase was not caused by gas contamination or by sewage pollution.

The following modified procedure for O.C. has been proposed for rapid field use. To 50 ml. samples of the water 1.5 ml. of exactly 0.0125N potassium permanganate and 5 ml. of 25 per cent sulfuric acid

solution are added. This solution is then placed in a boiling water bath for exactly 10 minutes. At the end of this period of digestion, the presence or absence of color is determined. If the solution is still colored, the water may be considered as satisfactory providing all the other criteria give no evidence of contamination. Samples which are colorless when removed from the bath should be considered as non-potable regardless of the results of other tests.

(6). Chlorine Demand. Most of the war gases react with chlorine and may be detected by routine determinations of chlorine demand. Chlorine demand is considered one of the most important methods of detecting gas contamination in water. The chlorine demand of the water may be defined as the quantity in parts per million of chlorine required to be added as chlorine water to produce a trace (0.1 p.p.m.) of residual chlorine after 5 minutes contact. The residual chlorine should ordinarily be determined by the ortho-tolidin method[6]. However, if the water to be tested contains more than 0.3 p.p.m. of Fe, 0.01 p.p.m. of manganic Mn and/or 0.3 p.p.m. of nitrite N, one of the modified procedures or the starch iodide procedure must be used. It should be understood, however, that the starch iodide-thiosulfate titration is not as sensitive for traces of residual chlorine and should not be used unless difficulties are encountered in the ortho-tolidin procedure.

REAGENTS

1. Ortho-tolidin solution. Dissolve 1 g. of ortho-tolidin in 1 liter of hydrochloric acid (180 ml. HCl sp.gr. 1.18 to 1.19 diluted to 1 liter). It is sometimes easier to dissolve the ortho-tolidin by grinding in 100 ml. of strong acid and then diluting to 1 liter with distilled water.

2. Chlorine water. By passing chlorine gas through distilled water a solution is made which contains slightly more than 1 g. of chlorine per liter. This solution is not stable and must be standardized each time it is used. A chloramine T solution containing 1000 p.p.m. of available chlorine may be used if desired.

Standardization. To 100 ml. of distilled water add 1 - 2 g. of KI crystals, shake until dissolved, add 5 ml. of chlorine water, 1 ml. of concentrated HCl and allow five minutes for liberation of the iodine. Then titrate with N/40 sodium thiosulfate using starch solution as an indicator. One ml. of N/40 sodium thiosulfate is equivalent to 0.886 mg. of chlorine, and mg. Cl_2 per ml. soln = ml. N/40 sodium thiosulfate X 0.886 ÷ 5.

Procedure

To a 250 ml. sample add the standard chlorine water (or chloramine T) 0.5 ml. at a time with gentle stirring until a spot plate test using 1 drop of ortho-tolidine solution and 0.25 ml. of sample gives a yellow color. If chloramine T is used one or two minutes will be required for the color to develop in each spot plate test. Call this the immediate

chlorine demand. On the basis of the immediate chlorine demand, take a new sample of smaller size if more convenient and add the proportionate total amount of chlorine solution added in the immediate determination plus 0.1 to 0.2 ml. in addition. Stir gently and in exactly five minutes test a portion of the sample for residual chlorine according to the standard method (7). Repeat this procedure until 0.1 p.p.m. residual chlorine is obtained after 5 minutes contact.

When 250 ml. of sample are used, the p.p.m. chlorine demand = ml. of Cl_2 soln. X mg. of Cl_2 per ml. X 4.

If more than 0.1 p.p.m. of residual chlorine is found after 5 minutes contact, an approximate value of the defined chlorine demand (if 250 ml. of sample were used) is equal to ml. of Cl_2 soln. X mg. of Cl_2 per ml. X 4 plus 0.1 minus the residual chlorine found in p.p.m. The chlorine demand may be used as a standard of potability. For this purpose, standard chlorine water may be used directly on the sample or if chloramine T is used the pH of the sample should be adjusted to 5 or less with a few drops of 6N sulfuric acid. Using this procedure, the chlorine demand of a potable water should not exceed 5.0 p.p.m. The only interfering substance for this test is hydrogen sulfide. If the odor indicates hydrogen sulfide, it may be removed by aerating the acidified water sample for a few minutes before the chlorine demand test is made.

A chlorine demand obtained in a clear water may indicate contamination by mustard, lewisite, ethyldichlorarsine or methyldichlorarsine. For the determination of these contaminants no adjustment of the pH is necessary. A chlorine demand in turbid waters may indicate diphenylchlorarsine (DA), diphenylcyanoarsine (CDA), or adamsite (DM), along with the above gases.

The chlorine demand obtained with chlorine water on samples of Cincinnati tap water contaminated with 500 p.p.m. of mustard (HS) was 513 p.p.m. and with 500 p.p.m. of lewisite (M-1) was 203 p.p.m. A procedure has been suggested for determining the chlorine demand at several pH values with chloramine T and interpreting the differences obtained in terms of mustard and possibly other gases. This procedure needs further study for confirmation.

(7) Arsenic. If members of Group 2 (the irritant smokes), lewisite ethyldichlorarsine and methyldichlorarsine of group 4 or arsenates and arsenites of group 6 are suspected, tests for arsenic should be made. A separate memorandum on the quantitative detection of arsenic in water by the standard Gutzeit method is attached hereto. Before the quantitative tests are carried out, one of the rapid qualitative tests may be made to determine whether the sample is heavily contaminated.

It is suggested that on any sample which has a high chlorine demand, a Reinsch test, a hydrogen sulfide test or the molybdenum blue test be made. The Reinsch test should be made as follows: To 100 ml. of sample on which the chlorine demand has been satisfied, add 16 ml. of conc. HCl (analytical reagent). Then add a 1/2 inch square of freshly

cleaned sheet copper*, cover the beaker with a watch glass and boil the liquid gently for 15 minutes. If arsenic is present, the surface of the copper will be darkened particularly at the edges. The same reaction is given by antimony and bismuth and some other metals. A water containing 500 p.p.m. of lewisite will completely blacken the copper in this test and a noticeable blackening will be obtained in concentrations down to about 20 p.p.m. of lewisite.

For the hydrogen sulfide test, take 20 ml. of the test solution and add 10 ml. of a freshly prepared, clear H_2S solution. If any of the arsenical vesicants are present in a concentration of about 20 p.p.m. or more, a white opalesence will be obtained by the formation of the arsine sulfide.

The Molybdenum Blue Direct Colorimetric Test for Arsenic

In the presence of the very small amounts of silicates and phosphates that are found in most water supplies, this test can be applied directly. The test is more sensitive than either of the other rapid tests for arsenic and can easily be adapted for use in the field. To detect arsenic contamination by vesicant or other arsenical gases the water sample should be oxidized with the permanganate solution used for the oxygen consumed determination with a sufficient excess to give a slight pink color to assure the complete oxidation of the arsenic. This also applied to inorganic arsenites. Reagents - same as given on page 7 of the following arsenic memorandum.*

Procedure

To 20 ml. or more of sample in a Nessler tube add 5 drops of concentrated sulphuric acid and add standard permanganate solution for the O.C. determination (0.4 g. per liter) a drop or two at a time until the first indication of permanganate remains. Dilute to 100 ml. with distilled water and proceed as directed following line 4, page 8, of the arsenic memorandum. A blue color developing within 10 to 30 minutes indicates arsenic. If a quantitative estimation is desired, arsenic standards should be prepared and treated simultaneously as directed on page 8 of the above memorandum.

(*) The copper may be cleaned in a few cc of nitric acid and then washed in tap water followed by distilled water.

(*) If desired, a stannous chloride solution may be used in place of the hydrazine sulfate. The stannous chloride stock solution contains 40 g. of C.P. $SnCl_2$ in 100 ml. of conc. HCl. Prepare a diluting HCl solution by diluting 40 ml. of conc. HCl to one liter. For the dilute stannous chloride, add 10 ml. of stock stannous chloride to 150 ml. of diluting HCl. One half ml. of dilute stannous chloride solution is substituted for the hydrazine sulfate in the procedure.

Cyanides

Because of the slight possibility of the introduction of hydrogen cyanide in water supplies by bombs or saboteurs, water works personnel should familiarize themselves with methods for detecting cyanides in water. Hydrogen cyanide in quantities up to 6 p.p.m. in a water supply would probably cause no difficulty. The average single fatal dose of cyanide by mouth for adults is 50 mgs. or more. There are a number of simple tests for the determination of cyanides in water. Among these are the prussian blue test, the benzidine-copper acetate test, the silver nitrate test, the phenolpthalin test, the gum guaiac-copper sulfate test and the ferric thiocyanate test. The methods to be described are the modified Schonbein-Sunberg gum guaiac test as a rapid qualitative test and the Fasken ferric thiocyanate procedure as a more sensitive quantitative method.

Modified Schonbein-Sunberg Test[9]

Reagents:

(1) Alcoholic gum guaiac - 0.1 g. of powdered gum guaiac is dissolved in 50 ml. of 95% ethyl alcohol. This reagent will keep about one week.

(2) Copper sulfate solution. Dissolve 1.0 g. of copper sulfate in 1 liter of distilled water and add 0.2 ml. of conc. H_2SO_4 (C.P.)

(3) Cyanide reagent - Mix 10 ml. of solution #1 with 3 ml. of solution #2. This reagent must be freshly prepared every two or three days.

(4) Strips of filter paper about 1 cm. by 10 cm. to be moistened in solution #3 when the test is made.

Procedure

Add 100 ml. of sample to be tested to an Erlenmeyer flask and acidify by adding conc. HCl one drop at a time until the water is acid to litmus. Insert a stopper carrying a thermometer in the flask and adjust so that the thermometer is immersed in the liquid. Heat the flask over a small flame until the liquid attains a temperature of 70°C. Dip a strip of the filter paper into the cyanide reagent (solution #3), immediately remove the stopper and thermometer from the flask and insert the test filter paper inside the flask so as to test the air above the liquid. If cyanide is present, the reagent moistened test paper should become blue within a few seconds. Steam interferes somewhat with the development of the color so the contents of the flask should not be heated to boiling. If the first test is negative, replace the stopper and thermometer; keep the contents of the flask at 70° C. for about 5 minutes and repeat the test again. A negative test indicates that cyanide is not present in toxic quantities.

Fasken's Ferric Thiocyanate Method[8]

Reagents:

(1) Yellow ammonium sulfide. Ordinary laboratory reagent.

(2) A 10 per cent sodium hydroxide solution. Dissolve 10 grams of C.P. sodium hydroxide in distilled water and make up to 100 ml.

(3) A 5 per cent hydrochloric acid. Dilute concentrated C.P. hydrochloric acid with distilled water to 5 per cent HCl by weight.

(4) A 10 per cent ferric chloride solution. Dissolve 10 grams of C.P. ferric chloride, $FeCl_3 6H_2O$, in distilled water and made up to 100 ml.

(5) Stock solution of potassium thoicyanate. Dissolve 4 grams of C.P. potassium thiocyanate in 1000 ml. of distilled water. Determine the exact strength of the solution by titration with N/10 silver nitrate and dilute with distilled water so that 1.0 ml. contains 1.0 mg. of CN, (1 ml. N/10 silver nitrate = 2.6 mg. CN).

(6) Diluted standard solution of potassium thiocyanate. Dilute 10 ml. of stock solution of potassium thiocyanate (reagent 5) with distilled water to 100 ml. One ml. of this solution is equivalent to 0.1 mg. CN.

Procedure

Five hundred ml. of the water is acidified with 0.5 grams of tartaric acid, distilled, and 50 ml. of distillate collected. The whole distillate or an aliquot containing less than 2 mg. CN is placed in an evaporating dish and 0.2 ml. of 10 per cent sodium hydroxide and 0.5 ml. yellow ammonium sulfide added. The mixture is evaporated just to dryness on the water bath. If the yellow color should fade at any time during the evaporation, a further drop or two of yellow ammonium sulfide is added. The residue is taken up with 10 ml. distilled water, 1.0 ml. of 5 per cent hydrochloric acid added, and the mixture heated just to boiling. It is then allowed to stand for some hours for the sulfur to coagulate, after which it is filtered and washed into a 50 ml. Nessler tube till about 40 ml. have passed through. A series of standard tubes is prepared containing from 0.2 ml. to 20 ml. dilute standard potassium thiocyanate solution, corresponding to from 0.02 mg. to 2 mg. cyanide, each of which is diluted to about 40 ml. and acidified with 1.0 ml. of 5 per cent hydrochloric acid. Now 1 ml. 10 per cent ferric chloride solution is added to each of the tubes and the volume adjusted to 50 ml. After mixing the colors are matched immediately.

If the amount of cyanide is above 0.1 mg. the test may be simplified by making fewer standards and comparing with the nearest in a colorimeter. While the color given by 0.01 mg. cyanide in 50 ml. is quite perceptible immediately after adding the ferric solution, it fades rather rapidly and comparison must be made at once. Hence this method is not recommended for amounts less than 0.05 mg. CN or 0.1 p.p.m. in the original water.

Chemical Detection of Chloropicrin in a Water Supply.

None of the common water tests already described will give any indication of chloropicrin in water. Hence, if contamination with chloropicrin is suspected, though the odor is not recognized, a chemical

confirmatory test should be made. Boiling a water sample with alcoholic potassium iodide decomposes the chloropicrin according to the following reaction:

$$CCl_3NO_2 + 4KI \longrightarrow CI_4 + 3KCl + KNO_2$$

The nitrite formed can then be detected with the ordinary nitrite reagents used in the water laboratory.

Procedure

To two ml. of the contaminated water sample in a test tube add 5 ml. of 5% alcoholic potassium iodide and heat to boiling. Cool and add 1 ml. of sulfanilic acid reagent and 1 ml. of alpha-napthylamine acetate reagent (reference 2, page 46). If the original water is nitrite free this procedure will detect chloropicrin to a concentration of about 3 p.p.m.

REFERENCES.

(1) Leitch, James L. Memorandum Report 31. General Factors in the Contamination of Water Supply Systems by Chemical Agents and Other Toxic Compounds. MD (EA). December 29, 1941.

(2) Drinking Water Standards, U.S. Public Health Service. (Soon to be published).

(3) Standard Methods of Water Analysis, Eighth Edition, American Public Health Association, pg. 64 (1936).

(4) Ibid. pg. 34 (1936).

(5) Ibid. pg. 136 (1936).

(6) Ibid. pg. 20, 166, 228-232 (1936).

(7) Ibid. pg. 164 (1936).

(8) Fasken, J. E. Jour. American Water Works Assn., 32, 487 (1940).

(9) Harger, R. N., Forney, Robert B. and Farr, Fred Jr. Simple Procedures for the Detection of Certain Chemical Contaminants in Drinking Water. Unpublished Memorandum (1942).

TABLE 5

CLASSIFICATION OF CHEMICAL AGENTS UPON BASIS OF TOXICITY TO WATER

Group 1	Agents which probably will produce a non-toxic water, though it may be non-potable.	Thermit, crude oil FS Mixture HC Mixture Titanium tetrachloride Carbon Monoxide	 FM
Group 2	Agents producing a turbid water which is non-toxic after removal of the turbidity.	Adamsite Diphenylchlorarsine Diphenylcyanoarsine	DM DA CDA
Group 3	Agents present in fairly high concentrations which would produce a non-toxic water.	Phosgene	CG
Group 4	Agents likely to cause trouble in a water supply unless extra precautions are taken.	Chloropicrin Mustard Lewisite Ethyldichlorarsine	PS HS M-1 ED
Group 5	Agents requiring additional data for definite classification.	Brombenzylcyanide Chloracetophenone CN Solution	CA CN CNS
Group 6	Compounds only likely to be used for deliberate contamination.	Arsenates, Arsenites Cyanides Heavy metal salts Alkaloids and toxins Pathogenic Bacteria	

TABLE 6
CHEMICAL BEHAVIOR OF AGENTS TO WATER

	Agent	Solubility mg. per liter at 20° C.	Behavior	Products of Hydrolysis	Treatment Required (3)
Vesicants	Mustard HS	800	Slowly hydrolyzed (1)	HCl and thioglycol (non-toxic)	Treatment for removal difficult. (2
	Lewisite M-1	500	Rapidly hydrolyzed	HCl and ClC_2H_2AsO (toxic, sparingly soluble)	May be used for pe iod of week or les if 10 p.p.m. are present.
	Ethyldichlorarsine ED	Very soluble	" "	HCl and C_2H_5AsO (toxic, soluble)	With higher concen trations pump to waste
Lung Injurant	Chloropicrin PS	1700	Stable	- -	- - - - - - - - - -
	Phosgene CC	1000	Rapidly hydrolyzed	HCl and CO_2	Neutralization if pH indicates it, otherwise no treat ment
Lacrimators	Brombenzylcyanide CA	Insoluble	Stable	- -	Probably coagulati and filtration is all that would be required.
	Chloracetophenone CN	"	"	- -	
Irritant Smokes	Adamsite DM	Insoluble	Stable	- -	
	Diphenylchlorarsine DA	Very slightly soluble	Slowly hydrolyzed	KCl and $(Ph_2As)_2O$	Coagulation and filtration
	Diphenylcyanoarsine CDA	Insoluble	Stable		
Screening Smokes	HC Mixture	- -	C_2Cl_6 slowly hydrolyzed		Neutralization wit $CaCO_3$ or lime, if pH indicates it, otherwise no treat ment required.
	SO_3 in $HClSO_3$ FS	Very soluble	Rapid reaction	H_2SO_4 and HCl	
	Titanium Tetrachloride FM	Soluble	Hydrolyzed	HCl and $Ti(OH)_4$	
Systemic Poison	Hydrocyanic acid	Very soluble	Slowly decomposed	Ammonium formate and brown polymeric products	Ferrous, ferric salt treatment followed by coagulation and filtration.

(1) Eighty-five (85) per cent of solute hydrolyzed within one hour.

(2) Best treatment involves use of high doses of activated carbon followed by coagulation and filtration followed by chlorination to beyond the break-point. If chlorine demand of treated water is over 5 p.p.m. water is unsatisfactory. For small doses (50 p.p.m. or less) of mustard, wait one hour and then take water from intermediate level for purification. Water containing 500 p.p.m. or more is not satisfactory for treatment.

(3) Standard disinfection practice with chlorine should be understood to follow all water treatment suggestions.

REPORT ON CONTAMINATED WATER EXAMINATION

Threshold odor limit found for chloropicrin in water was ________ p.p.m.

Results on Contaminated Cincinnati Tap Water

Sample	Control Tap Water	Unknown #1	Unknown #2	Unknown #3	Unknown #4
Odor if any	None				
pH	7.6 to 7.8				
Chlorine Demand (5 minute contact)	Less than 1 p.p.m.				Less than 1 p.p.m.
Arsenic	None found				None found
Gas Suspected					
On basis of above tests is water potable?	Yes				

Name ________________________________

4-0998-P 60-BU-COS-WP

LABORATORY PROBLEMS

Detection of Gas Contamination in Water

(1) Determine threshold odor limit on Chloropicrin series and record on report sheet. Then analyze the following water samples as suggested.

Unknown #1

This sample contains 400 p.p.m. of an arsenical. Notice absence of odor. Determine pH and check arsenic by Reinch test. This sample has a high Cl_2 demand.

Unknown #2

Determine pH and chlorine demand and arsenic by molybdenum blue method.

Unknown #3

Determine pH and chlorine demand and arsenic by molybdenum blue method.

Unknown #4

Determine the odor and pH. If odor is recognized record contaminant.

MEMORANDUM ON THE DETECTION AND ANALYSIS OF ARSENIC IN WATER CONTAMINATED WITH CHEMICAL WARFARE AGENTS

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Some of the arsenical compounds which may be used in chemical warfare and contaminate water supplies include the following:

Name	Formula	Chemical Warfare Symbol
1. Methyldichlorarsine	CH_3AsCl_2	MD
2. Ethyldichlorarsine	$C_2H_5AsCl_2$	ED
3. Phenyldichlorarsine	$C_6H_5AsCl_2$	
4. Diphenylchlorarsine	$(C_6H_5)_2AsCl$	DA
5. Lewisite-Chlorovinyldichlorarsine	$ClCH{:}CHAsCl_2$	M-1
6. Diphenylaminocyanoarsine	$NH(C_6H_4)_2AsCN$	
7. Diphenylcyanoarsine	$(C_6H_5)_2AsCN$	CDA
8. Adamsite-Phenarsazine Chloride	$NH(C_6H_4)_2AsCl$	DM

The first five of these compounds are hydrolyzed in water to form the corresponding arsenious oxides. These reactions are illustrated in the following equations:

(2) $C_2H_5AsCl_2 + HOH \quad C_2H_5AsO + 2HCl$

(5) $ClCH{:}CHAsCl_2 + HOH \quad ClCH{:}CHAsO + 2HCl$

Although some of these arsenicals hydrolyze in water, it is necessary to break down the hydrolysis product before the arsenic can be detected quantitatively by most methods of analysis. However, with arsenicals in solution and hydrolyzed the bromate method can be used to titrate arsenic directly (page 11) without any preliminary preparation of the sample. With contamination by methyldichlorarsine, ethyldichlorarsine and Lewisite and in the practical absence of phosphate and silica the molybdenum blue method can be used directly after the water sample is oxidized with permanganate in a slightly acid solution. With contamination by arsenicals which are less soluble and more stable, such as

Diphenylaminocyanoarsine and Adamsite, the sample must be prepared for analysis by digestion. Hence, it is advisable to digest all water samples suspected of being contaminated with arsenicals and after digestion apply the Gutzeit or alternate tests as described hereafter.

Preparation of Sample by Digestion.

1. Reagents

Sulfuric Acid - C.P. Analytical Reagent.

Nitric Acid - C.P. Analytical Reagent.

2. Procedure

To a 500 ml. water sample in an 800 ml. Kjeldahl flask add 10 ml. of C.P. sulfuric acid, one ml. of C.P. nitric acid and a small piece of ignited pumice. Mix by shaking and digest under a hood until fumes of sulfuric acid are given off. After cooling 50 ml. of distilled water are added and the digestion is continued until sulfuric acid fumes are again obtained. Cool and add 10 ml. of water and transfer to a 50 ml. or 100 ml. volumetric flask. Rinse the Kjeldahl flask with water and add to the volumetric flask, making the sample up to 50 ml. or 100 ml. Proceed to the analysis by one of the following procedures.

The Gutzeit Official AOAC Method (1940 Edition).

Reagents

(a) Stannous chloride solution. Dissolve 40 gm. of As - free $SnCl_2.2H_2O$ in HCl and make up 100 ml. with same strength acid.

(b) Zinc. Use 20-30 mesh, As - free granulated zinc which needs no preliminary treatment.

(c) Ammonium oxalate solution - saturated.

(d) Potassium iodide solution - Dissolve 15 gm. KI in H_2O and dilute to 100 ml.

(e) Sand. Clean 30 mesh (through 30 - but not 40 mesh) white sea sand by washing successively with hot 10 per cent N_aOH solution, hot concentrated HNO_3, and hot distilled H_2O. Dry the clean sand.

(f) Mercuric bromide paper. Use commercial arsenic papers cut from paper of uniform weight and texture into strips exactly 2.5 mm. wide and about 12 cm. long. (Uniformity in width and texture of paper are of great importance in this comparison method. Irregular texture produces irregular impregnation, with consequent inaccurate results). To sensitize, soak strips one hour or longer in 3 - 6 per cent (optimum 5 per cent) solution of filtered $HgBr_2$ in alcohol, according

to quantity character and activity of zinc used. (Attenuated, unsatisfactory stains, due to over-rapid evolution of arsine can be shortened and intensified by increasing concentration of $HgBr_2$ and vice versa). If the strips are in sheets cut off two sides before soaking and leave strips attached at ends. After sensitization remove strips and dry individual ones on glass rods and groups by waving in the air. Place strips when nearly dry between clean sheets of paper and subject them to pressure long enough to take out bends and curls. Store in dry dark place. (Aging of paper usually results in markedly fainter and longer stains. Desirable types of stains result from use of impregnated strips not over two days old). When ready to use, cut individual strips off squarely half inch from one end and insert this end in the narrow tube of the apparatus. Handle sheets by the paper attached to either end and cut in half just before use. Strips must be clean and free from any contamination.

(g) Standard arsenic solution. Dissolve 1 gm. As_2O_3 in 25 ml. 20 per cent NaOH. Saturate solution with CO_2 and dilute to 1 liter with recently boiled distilled water. One (1) ml. of this solution contains 1 mg. As_2O_3. Dilute 40 ml. of this solution to 1 liter. Make 50 ml. of the diluted solution to 1 liter and use to prepare standard stains. A solution containing .001 mg. As_2O_3 may also be prepared. Prepare fresh dilute solution at frequent intervals.

Apparatus.

(a) Generators and absorption tubes.

Use 2 oz. wide-mouthed bottles of uniform capacity and design as generators and fit each by means of perforated stoppers with a glass tube 1 cm. in diameter and 6 - 7 cm. long, with an additional constricted end to facilitate connection. Place small wad of glass wool in constricted bottom end of tube and add 3.5 - 4 gm. of the 30-mesh cleaned sand, taking care to have the same quantity in each tube. Moisten sand with 10 per cent Pb acetate solution and remove excess by light suction. Clean sand when necessary by treatment (do not remove sand from tube) with HNO_3 followed by H_2O rinse and suction. Treat with Pb acetate solution. If sand has dried through disuse, clean and remoisten it as directed. Connect tube by means of rubber stoppers with narrow glass tube 2.6 - 2.7 mm. in internal diameter and 10 - 12 cm. long, and introduce the clean end of the strip of $HgBr_2$ paper. (A 3 mm. bore allows the paper to curl, which results in an uneven stain and poor end-point). Clean and dry tube before inserting bromide paper. (An ordinary pipe cleaner may be used).

Water Bath. Use any constant temperature water bath. If no water bath is available, use any flat bottomed container of suitable depth and capacity. (A deep water bath is suggested to insure uniform conditions during evolution and absorption of arsine).

Determinations.

Determine the acid by titration in a definite aliquot of the digested sample solution. Place aliquot containing 0.01 mg. - 0.03 mg.

As_2O_3 (.020 - .025 mg. is optimum) and not larger than 30 ml. in Gutzeit generator. If arsenic in aliquot taken is outside limits specified, repeat with proper aliquot. On the basis of the acidity titration neutralize the sulfuric acid in the aliquot with a 25 per cent solution of sodium hydroxide, cool and add exactly 5 ml. of concentrated HCl. Cool when necessary and add 5.0 ml. KI reagent and 4 drops of the $SnCl_2$. Prepare standards corresponding to 0.01, 0.02 and 0.03 mg. As_2O_3 from reagent (g). Since standards must contain same kind and amounts of acid as samples, add 5 ml. of HCl, and as H_2SO_4 has been neutralized, add an equivalent quantity As - free Na_2SO_4 to standards. Mix and allow to stand 30 minutes at not less than 25° or 5 minutes at 90°. Dilute with H_2O to 40 ml.

Prepare generator as directed under 2 and center strip of $HgBr_2$ paper carefully in narrow tube. According to activity of zinc, add 2 - 5 gm. granulated zinc adding same quantity to each generator.

Immerse the apparatus within 1 inch of top of narrow tube in water bath (constant temperature of 20° - 25°) allow evolution to proceed 1.5 hours. Compare strips or prepare graph from standard strips.

Molybdenum Blue Method* (Alternate)

Reagents.

1. Standard Arsenious Oxide Solution. Dissolve 0.3241 gm. of arsenic trioxide, As_2O_3, in 25 ml. 10 per cent sodium hydroxide solution, make slightly acid with sulfuric acid (1:6) and dilute with water to 1 liter.

2. Ammonium Molybdate Solution. Dissolve 25 gm. ammonium molybdate in 300 ml. water. Dilute 75 ml. of concentrated sulfuric acid to 200 ml. with water and add to the ammonium molybdate solution.

3. Sodium Hyposulfite solution. Two (2) gm. sodium hyposulfite dissolved in water and diluted to 100 ml.

4. Hydrazine sulfate solution, half saturated. Shake excess hydrazine sulfate with 50 ml. water until no more dissolves, filter and dilute filtrate with equal volume of water. Follow the method for digesting and preparing the sample heretofore described for the official Gutzeit method.

A Gutzeit generator is prepared in the usual way, but instead of the tube containing the mercuric bromide paper, attach another tube leading the generated gases to a trapping device containing 3 ml. of sodium hypobromite solution (3 ml. bromine water plus 1 ml. 0.5 N NaOH solution) as shown in the accompanying figure. It is better to have 2 trapping devices in series, the second need contain only water. Treat the arsenic test solution in the same way as in the Gutzeit method.

(*) For a complete discussion of this method see Colorimetric Microdetermination of Arsenic by Jacobs and Naylor, Ind. & Eng. Chem., Anal. Ed., Vol. 14, No. 5, p. 442 (1942).

Allow the generation of arsine to proceed as directed under the Gutzeit method. After generation is complete, transfer the contents of the traps to a graduated colorimeter tube, Nessler tube or volumetric flask. Wash the trap with 6 two ml. portions of water using an aspirator to blow the wash solution out of the bead traps. Add 5 drops of concentrated sulfuric acid and stir. Add 1 ml. of ammonium molybdate solution and shake. Add 1 ml. of a half saturated solution of hydrazine sulfate or 1 ml. sodium hyposulfite solution. The hyposulfite solution must be prepared at least 24 hours in advance and should not be used until then. Freshly prepared hyposulfite solution causes a turbidity which can be removed by filtration but the method works best when the reagent is prepared as directed, or with hydrazine sulfate.

Make to volume. Allow to stand for 0.5 hour for full developement of the blue color. Compare with standards treated in a similar way at the same time.

The standards are prepared from the stock arsenic solution. Add 3 ml. of hypobromite solution to the aliquot selected for the standard or standards, dilute to 17 ml., add 5 drops concentrated sulfuric acid, stir, add 1 ml. of molybdate solution, stir, add 1 cc. of half-saturated hydrazine solution, stir and make up to same volume as test solution.

To develop the proper quality of color in the test solution and to inhibit the development of color in the blank, it is necessary to add the proper amount of acid. If the final dilution is less than 20 - 25 ml., add less sulfuric acid; if the final dilution is greater than the aforementioned volume add more sulfuric acid.

(Note: The Chaney Method (Jour. Ind. Eng. Chem., Anal. Ed., Volume 12, p. 691 (1940)) is a modification of the molybdenum blue method which requires a special glass digester and still. Where this equipment is available the procedure is permissible).

<u>BROMATE METHOD - ALTERNATE</u> (Tentative Method, AOAC., 1940 Ed.).

Applicable to the determination of arsenic in plants and food products where a sample of convenient size for digestion will yield at least 0.324 mg. As_2O_3.

<u>Reagents.</u>

<u>1. Ammonium oxalate - urea solution.</u> To a saturated solution of ammonium oxalate add 50 gm. urea per liter.

<u>2. Hydrazine sulfate - sodium bromide reagent.</u> Dissolve 20 gm. hydrazine sulfate and 20 gm. sodium bromide in 1 liter dilute hydrochloric acid (1 pt. HCl ; 4 pts. water).

<u>3. Sodium chloride - commercial salt, uniodized.</u>

4. Standard potassium bromate solution. Dissolve 0.1823 gm. $KBrO_3$ in water and dilute to 1 liter. Standardize by titration against standard As_2O_3 solution, making the titration at about 90° and in the presence of 100 ml. H_2O and 25 ml. HCl in order to simulate conditions under which the samples will be titrated. One (1) ml. $KBrO_3$ solution should be equivalent to 1 ml. As_2O_3 solution.

5. Standard As_2O_3 solution. Dissolve 0.3241 gm. As_2O_3 in 25 ml. 10 per cent NaOH, make slightly acid with H_2SO_4 (diluted with 6 parts of water) and dilute to 1 liter with water.

Distilling apparatus.

The distillation apparatus consists of an 800 ml. Kjeldahl flask, a distilling tube and a 300 ml. Erlenmeyer flask as a receiver.

To prepare the distilling tube bend 10 - 15 mm. glass tubing to an acute angle of about 70°. Draw the longer arm, which is about 15 - 20 inches long down to an orifice of approximately 3 mm. Fit the shorter arm (about 4 inches) with a one-hole rubber stopper to fit the Kjeldahl flask. The stopper is to be previously boiled for 15 minutes in 10 per cent NaOH solution and then in HCl for 15 minutes in order to remove sulfur compounds which might be distilled and react with the bromate solution.

Preparation of Sample.

Introduce 500 ml. water sample containing 0.324 mg. or more of As_2O_3 into an 800 ml. flask. Proceed with acid digestion as follows:

Add 20 ml. H_2SO_4 or (rarely) if material is difficult to digest, 25 ml. at the beginning of digestion. After digestion is complete add 50 ml. H_2O and 25 ml. ammonium oxalate-urea solution and boil until white SO_3 fumes extend into the neck of the flask to decompose the oxalates and urea completely (volatile intermediate products may distil and react with the bromate). If the heat available is insufficient to decompose these substances, it is preferable to evaporate to fumes after the addition of water alone. Hydrazine sulfate will destroy small amounts of nitrogen oxides.

Isolation.

Add 25 ml. water to the digested solution in the Kjeldahl flask and cool to room temperature. Place 100 ml. water in Erlenmeyer flask and set up apparatus so that the long arm is well under the surface of the water in the Erlenmeyer flask. Add 20 gm. NaCl and 25 ml. hydrazine sulfate-sodium bromide solution, to the Kjeldahl flask and connect the distilling tube. Heat the flask over a small well protected flame and distil into the water in the Erlenmeyer flask. (Heating is not intended to bring about boiling but to bring about evolution of HCl gas which carries over $AsCl_3$ with it. Absorption of the HCl gas by the water causes

a rise in temperature which indicates progress of distillation). Adjust the flame so that the temperature of the distillate solution will rise to 90° in 9 - 11 minutes, and then disconnect the distillation apparatus. (The residual mixture in the flask should be not less than 55 ml.). If distillation proceeds further or larger quantity of sulfuric acid is used than that specified in digestion, sulfur dioxide is distilled which is titrated as arsenic).

Determination.

Titrate the distillate at once with the bromate standard solution using 3 drops methyl orange indicator (0.5 gm. M.O. per liter water). (Single drops of the indicator not exceeding three may be added during the course of the titration). Toward the end of the titration add the bromate very slowly and with constant agitation to avoid local excess. The end point is reached when a single drop of bromate just destroys the final tinge of red color. Use an Erlenmeyer flask containing distilled water alone as a reference. (The end point must not be overrun as the action of the indicator is not reversible and back titration is not reliable. At the proper end point the red color produced by 2 additional drops of methyl orange indicator should persist for at least 1 minute). Correct the results for the volume of bromate used in blank run. For this purpose digest 5 gm. sucrose with the same quantity of reagents and use the regular distillation procedure. (Blank titration should not exceed 0.7 ml. The method is accurate down to the variations in the blank which should not exceed 0.1 ml. when reagents from the same lot are used). Should the blank titration be high or variable, test the individual reagents for purity by a bromate titration. Test the sulfuric acid by bringing 20 ml. to a boil, cool, dilute with H_2O to 100 ml., add a little HCl and titrate while hot. It probably will furnish most of the blank. Select rubber stoppers carefully as these are often the source of unsatisfactory blanks.

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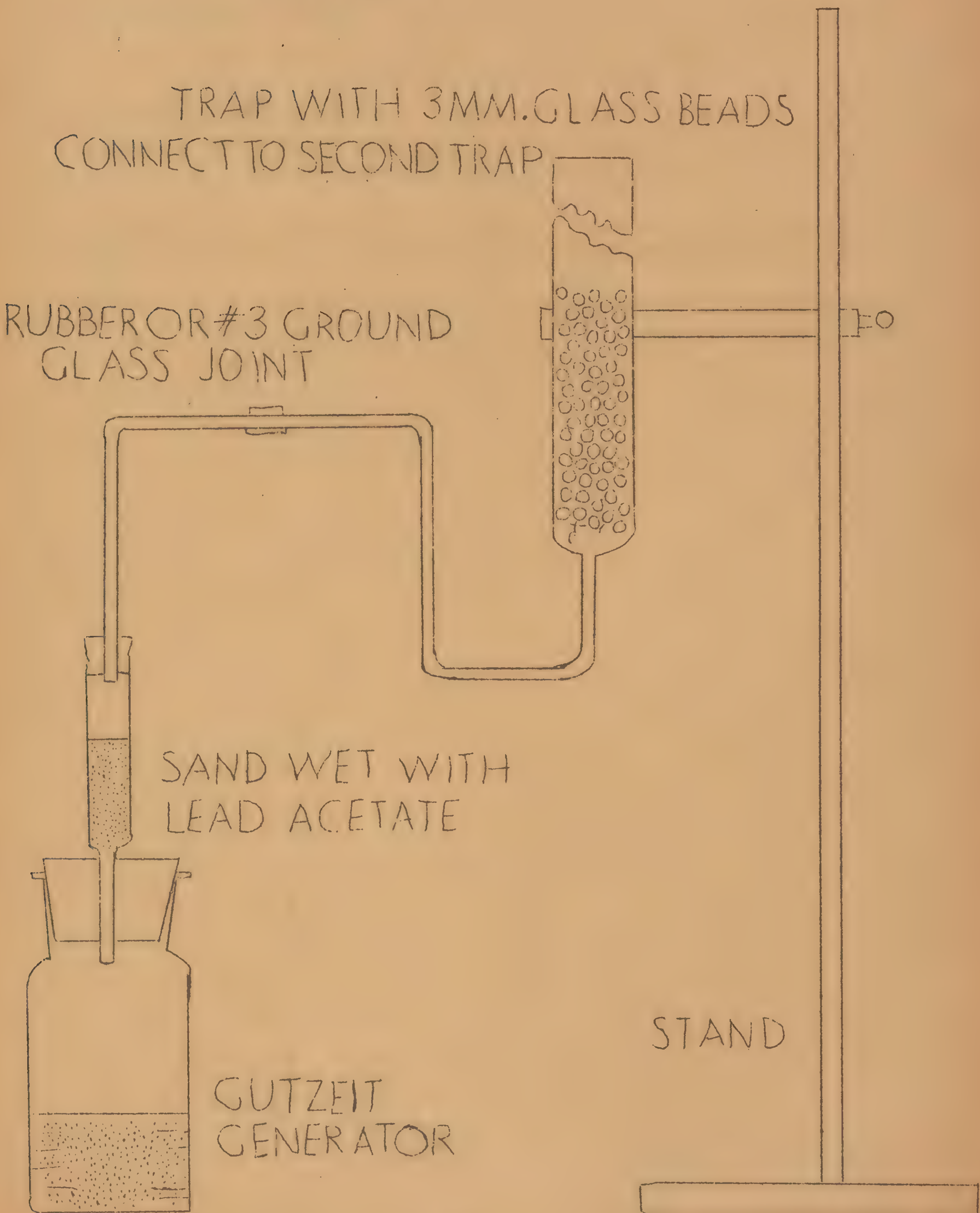
APPARATUS FOR THE

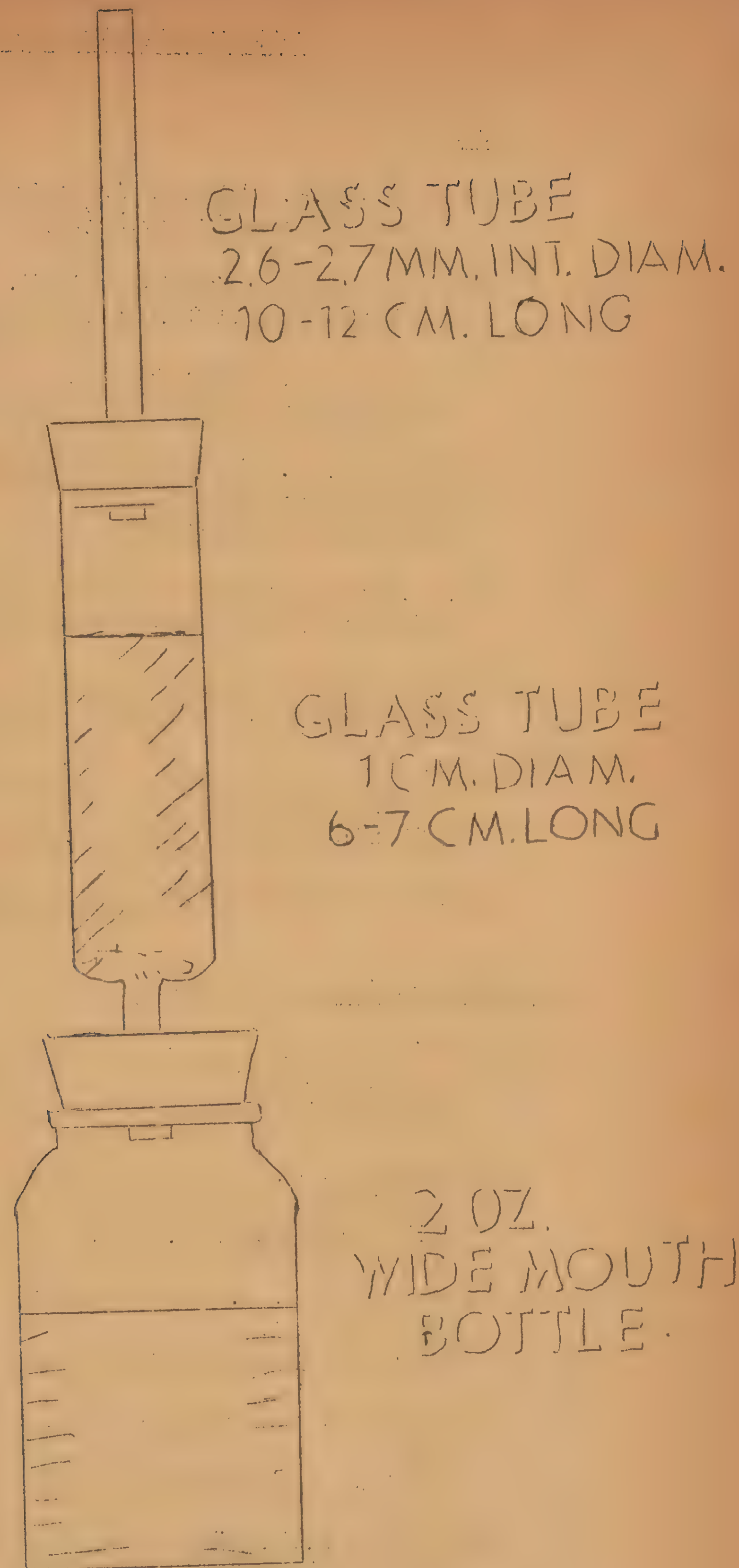
MOLYBDENUM BLUE

METHOD.



GUTZEIT

GENERATOR



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THE DETECTION OF WAR GASES IN FOODS

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General Considerations

I. Cases where tests need not be made for presence of gas in foods.

A. Properly packaged foods in containers impervious to gas, as described in previous discussion; outside only of containers need be decontaminated.

B. Some foods should be destroyed without analysis, as milk in open vessels, or in bottles with cardboard caps which have been splashed with liquid gas; or vegetables or eggs which have been splashed.

II. Types of contamination

A. By liquid spray or splashing, or by arsenical smokes.

B. By exposure to a gaseous atmosphere; foods in this class may be rendered partially or completely usable, while those in class A can seldom be used. Where mustard gas or lewisite has been used, butter, fats, cheese, and meats should receive special attention, and should be considered as always belonging to class A.

III. Subjective examination

A. Note appearance, odor, color, presence of visible stains on foods.

B. Note location of food with respect to visible signs of area of gassing.

C. If chemical smokes have been used, examine the surface layers of the food microscopically for the presence of appropriate solid particles.

D. Apply cautious palatability tests only in the absence of all positive indications of contamination.

E. Where mustard gas or lewisite is the suspected contaminant chemical examination should always be carried out.

F. The possibility of mixed gases should always be kept in mind.

G. Growing crops contaminated by mustard gas or lewisite show scorching and bleaching; in the case of the former gas, the fresh growth on the plants after they have recovered will be wholesome. Lewisite and other arsenicals, however, complicate the problem because of the residual arsenic; the plants should not be used until after the arsenic content has dropped to safe limits.

IV. Sampling for chemical analysis

A. For initial identification of gas, use grossly contaminated exposed surface layers of food, or actual droplets or splashes of the liquid gas, absorbed on filter paper or cotton.

B. To determine usability of the food, tests should be made on large samples of foodstuffs (approximating that eaten in a meal).

1. Take sample by cutting thin slices from suspected portions and placing them in clean, dry jar, fitted with a screw cap.

2. Separate samples should be taken from the surface and from interior portions of the food, using different sample jars.

3. The knife or other utensil must be cleaned between each cut, using a bleaching powder-water paste; all bleaching powder must be removed from the knife before touching the food.

C. Proper precautions should be taken to prevent exposure of the analyst to the gas.

V. Chemical analysis

A. Air-flow analysis; apparatus consists of a large container fitted with a stopper carrying glass inlet and outlet tubes, with a supply of air purified by passage through granular activated charcoal and anhydrous calcium chloride. The container is kept at a temperature of about 37° C. by a water bath. Aspiration of air is carried out at the rate of 0.1 to 0.5 liter per minute, for 10 to 15 minutes, into 10 ml. of absorbent liquid. The first aspiration is made into water, then a second aspiration into alcoholic potassium hydroxide is carried out. The liquids are examined according to the following Qualitative Analysis Procedure, Parts I and II.

B. A fresh portion of the sample is extracted with hot absolute alcohol; the extract is then examined according to the Qualitative Analysis Procedure, Part III.

Rapid "Sorting Test"

The alcoholic potassium hydroxide solution through which air from the sample was passed in the air-flow analysis (second aspiration in V-A above) can, if desired, be put through a rapid "sorting test" which may shorten the analytical procedure. After acidification (nitric acid) test separate portions for halides and cyanide (precipitation with silver nitrate), nitrite (red color with Griess-Ilosvay reagent), and arsenite (Gutzeit test). If definite positive indications are given by one or more of these tests, it may be possible to proceed directly to the Confirmatory Tests (p. 6). However, the following complete Qualitative Analysis Procedure is recommended for use whenever time permits.

Classification of the War Gases

The war gases may be grouped according to the elements present, ignoring carbon, oxygen, and hydrogen. The standard tests for the particular elements involved may be applied in order to aid identification of a gas.

I. Halogen only - Chlorine, phosgene, diphosgene, benzyl and xylyl bromides, bromoacetone, chloroacetophenone, ethyl iodoacetate.

II. (a) Sulfur only - Hydrogen sulfide, dimethyl sulfate.

(b) Sulfur and Halogen - Mustard gas, thiophosgene, perchloromethyl mercaptan, sulfuryl chloride.

III. (a) Nitrogen only - Hydrocyanic acid.

(b) Nitrogen and Halogen - Chloropicrin, bromobenzyl cyanide, phenyl carbylamine chloride, cyanogen halides.

IV. (a) Arsenic only - Arsine.

(b) Arsenic and Halogen - Lewisite, methyl and ethyl dichloroarsines, diphenyl chloroarsines, arsenic trichloride.

V. Arsenic, Halogen, and/or Nitrogen - Diphenyl cyanoarsine, diphenylamine chloroarsine.

Qualitative Analysis Procedure

I. Aspiration into water

A. The aqueous solution contains a precipitate - indicates presence of $SnCl_4$, $TiCl_4$, $SiCl_4$, diphenyl urea (from phenyl carbylamine chloride) or sulfur (from perchloromethyl mercaptan).

B. After filtration (if necessary) test a portion of the filtrate with silver nitrate, acidified with nitric acid.

1. Precipitate - indicates presence of diphosgene, mustard gas, lewisite, or other readily hydrolyzable gases.

2. No precipitate - absence of gases covered in this section (I),

except for those in C-4-b and C-6 below; test for them, then proceed to next section (II).

C. If a precipitate occurred in B, test separate portions of the original filtrate as follows:

1. Add a few drops of hydrogen sulfide water

   (a) Turbidity - indicates presence of alkyl chloroarsines

   (b) Turbidity, which dissolves in excess - indicates presence of lewisite

   (c) Sulfur precipitate - indicates presence of cyanogen chloride or bromide

   (d) Oily suspension of phenyl isothiocyanate - indicates presence of phenyl carbylamine chloride

2. Add a drop of 1% phenol solution and run in carefully a layer of concentrated sulfuric acid; a red zone at the interface (due to formaldehyde) indicates the presence of chloromethyl chloroformate or a halogen-substituted methyl ether.

3. Add sodium hydroxide solution and warm; test the air above the liquid with moistened litmus paper for ammonia; a positive test indicates the presence of cyanogen halide.

4. Add barium chloride solution acidified with hydrochloric acid

   (a) White precipitate of barium sulfate; this sample also gave a positive test with silver nitrate above - indicates the presence of chlorosulfonic acid or ester, or sulfuryl chloride.

   (b) White precipitate of barium sulfate; this sample did not give a positive test with silver nitrate above - indicates the presence of sulfur trioxide or dimethyl sulfate.

5. Add lead acetate solution; a black precipitate of lead sulfide indicates the presence of thiophosgene or perchloromethyl mercaptan.

6. Carry out the standard Gutzeit test for arsenic; a positive test greater than the reagent blank, indicates the presence of arsenic trichloride, lewisite, or ethyldichloroarsine.

II. Aspiration into alcoholic potassium hydroxide solution (10-20%)

Warm and then cool the solution; acidify where necessary and test separate portions as described under I above, then test other portions as follows:

A. Acifidy with nitric acid and add silver nitrate solution; a yellow precipitate of silver bromide indicates the presence of bromine-containing lachrymators, as bromobenzyl cyanide.

B. Acidify with acetic acid and test with Griess-Ilosvay nitrite reagent (see below for details); a red color, deeper than the reagent blank, indicates the presence of chloropicrin.

Griess-Ilosvay Reagent: (1) Dissolve 1 g. of sulfanilic acid in hot water containing 14.7 ml. of glacial acetic acid and dilute to 300 ml. with water. (2) Dissolve 0.2 g. of a-naphthylamine in water containing 14.7 ml. of glacial acetic acid and dilute to 350 ml. with water. Use equal parts of each solution; about 2 ml. of the mixture is sufficient for the test.

III. Tests for persistent lachrymators

Macerate the sample; extract it with hot absolute alcohol for several minutes, then filter and test the filtrate. Add alcoholic potassium hydroxide to the filtrate and warm it. An intense red color accompanied by the formation of resinous products, indicates the presence of chloro- or bromoacetone. Filter, if necessary, and test separate portions of the filtrate as follows:

A. Acidify with nitric acid and add silver nitrate solution; a white precipitate of silver chloride indicates the presence of diphosgene, mustard gas, lewisite, or other readily hydrolyzed gases.

B. Boil a portion of the filtrate and test the air above the liquid with moistened litmus paper for ammonia; a positive test indicates the presence of bromobenzyl cyanide or cyanogen halide.

C. Evaporate the alcohol at a low heat and treat the residue with hot alkaline potassium permanganate solution. Acidify the solution with dilute sulfuric acid and extract it with ether. Allow the ethereal extract to evaporate spontaneously.

1. Dissolve one portion of the residue in water and add a drop of ferric chloride solution; a buff-colored precipitate, due to benzoic acid, indicates the presence of benzyl bromide, bromobenzyl cyanide, or chloroacetophenone.

2. Add concentrated sulfuric acid containing a little resorcinol to another portion of the residue; a greenish-red color, which shows a decided green fluorescence in alkali, indicates the presence of xylyl bromide. This color is caused by fluorescein, formed by the phthalic acid resulting from the oxidation of xylyl bromide.

D. Acidify with acetic acid and divide the solution into two parts.

1. Test one portion with silver nitrate solution for bromide or iodide.

2. Add a crystal of guaiacol and a few drops of concentrated sulfuric acid to the other portion. A violet color, due to glycollic acid, indicates the presence of ethyl iodoacetate or ethyl bromoacetate; this should also be confirmed in test 1 just above.

Regardless of whether lewisite or other arsenicals are detected after aspiration according to the qualitative analysis procedure, the arsenic content of the food itself should always be determined if contamination with a war gas is suspected. This arsenic determination can be adequately done by the Gutzeit method as described in the Methods of Analysis of the Association of Official Agricultural Chemists, Fifth Edition, p. 390 (1940). Concentrations of arsenic significantly greater than those normally expected in the type of food investigated may have resulted from hydrolysis of the arsenical war gases; if the hydrolysis is sufficiently complete, these gases would probably not be detected in the above qualitative analysis scheme. Decisions regarding the usability of the food must therefore be based not only on the subjective examination and the results of the qualitative analysis, but on the concentration of arsenic in the food itself.

If contamination with hydrogen cyanide is suspected, a test should be carried out by aspiration of the air through benzidine copper acetate paper. A blue color indicates the presence of cyanide.

Benzidine copper acetate paper: Two to three g. of pure benzidine acetate are heated to 80° C. in 100 ml. of distilled water for 10-15 minutes, with constant shaking. The filtered solution is mixed with one-twelfth its volume of cupric acetate solution (3 g./100 ml.) immediately before the test; the test paper is dipped into this mixture, allowed to drain, and dried until only just moist.

Confirmatory Tests

The presence of any gas indicated by positive results in the Qualitative Analysis Procedure should always be confirmed by one of the following tests. These confirmatory tests can be carried out on test solutions or on filter papers impregnated with a reagent through which air from the preceding air-flow analysis can be drawn. A convenient holder for the test papers consists of two glass tubes with ground ends, which are fitted tightly into wooden blocks connected by a steel spring. The tension of this spring holds the ground glass ends together, with the test paper being inserted between them.

Phosgene and Diphosgene: Five grams of p-dimethylaminobenzaldehyde and 5 g. of diphenylamine are dissolved in 100 ml. of alcohol. Filter paper moistened with this reagent gives a yellow or orange color in the presence of phosgene or diphosgene. Chlorine or hydrochloric acid must first be removed from the air used for the test by a guard tube containing sodium thiosulfate and sodium iodide.

Mustard Gas: The gas is aspirated into a 1% solution of B-naphthol in 0.1 N aqueous-alcoholic (50:50) alkali. A white turbidity, forming after 10-15 minutes or on warming (due to the di-B-naphthyl ether) indicates the presence of mustard gas.

A characteristic and sensitive test consists of passing the air through one or two drops of 0.1% gold chloride solution; a yellow colloidal turbidity is formed if mustard gas is present.

Lewisite and Primary Dichloroarsines: The air is aspirated into a small quantity of water and two or three drops of hydrogen sulfide water are added. An opalescence or turbidity indicates a primary dichloroarsine; if the turbidity is soluble in excess, lewisite is present.

A specific, although not very sensitive, reaction of lewisite consists of treatment of a small drop of the liquid with cold 15% sodium hydroxide. Acetylene which is liberated can be detected by a red stain on ammoniacal cuprous chloride paper, while the reaction liquid will contain arsenite (detected by the Gutzeit test) and chloride (detected by silver nitrate).

Cyanogen Chloride or Bromide: The air is aspirated through a paper soaked in saturated sodium sulfide solution and used moist. One drop of concentrated hydrochloric acid followed by a few drops of 1% ferric chloride solution are "spotted" on; a red color indicates the presence of cyanogen halide.

Phenyl Carbylamine Chloride: The air is aspirated into water and the solution is boiled. A white precipitate of diphenyl urea indicates the presence of phenyl carbylamine chloride.

Chloromethyl Chloroformate: Use the test given in the Qualitative Analysis Procedure.

Chlorosulfonic Acid or Ester, or Sulfuryl Chloride: Aspirate the air into hot water; the presence of both free hydrochloric and sulfuric acids (acid solution, barium chloride test, silver nitrate test) characterizes these gases.

Dimethyl Sulfate: Boil the contaminated sample with water under a reflux condenser for one hour and then distil. If the first portion of the distillate contains methyl alcohol (test according to U. S. Pharmacopoeia XI, p. 355, methanol test in whisky) together with a positive sulfate test in the Qualitative Analysis Procedure, dimethyl sulfate is present.

Perchloromethyl Mercaptan: Aspirate the air into hot water; the evolution of carbon dioxide, and the presence of hydrogen sulfide (lead acetate test) and hydrochloric acid (silver nitrate test) with the precipitation of sulfur on boiling, indicates that perchloromethyl mercaptan is present.

Thiophosgene: Aspirate the air into water; the presence of hydrogen sulfide (lead acetate test) and hydrochloric acid (silver nitrate test) indicates that thiophosgene is present.

Bromobenzyl Cyanide: (1) The liquid gas gives a deep red color with concentrated sulfuric acid.

(2) The air is aspirated into 10% silver nitrate solution and the mixture is boiled. Reduction of the silver nitrate (with a precipitate) and the formation of benzaldehyde, which can be detected by its characteristic odor, indicates the presence of bromobenzyl cyanide.

Chloropicrin: The air is aspirated through filter paper which has been impregnated with a 10% solution of dimethylaniline in benzene and dried. A yellow or maroon color indicates the presence of chloropicrin.

Benzyl Bromide: Aspirate the air directly into hot alkaline potassium permanganate solution and treat the mixture as described in the Qualitative Analysis Procedure.

Chloroacetophenone: If the alcoholic extract in Part III of the Qualitative Analysis Procedure contains an appreciable amount of gas, 20% aqueous-alcoholic (50:50) sodium sulfide is added, the mixture is warmed, cooled, and diluted with water. The chlorine is removed from the compound by this treatment and the corresponding sulfide (m.p. 77° C.) is precipitated.

Xylyl Bromide: Use the test given in the Qualitative Analysis Procedure.

Ethyl Iodoacetate or Ethyl Bromoacetate: Aspirate the air directly into warm alcoholic potassium hydroxide solution and apply the test described in the Qualitative Analysis Procedure.

Possible Interferences

Certain substances often present in foods can give tests which may be mistaken for some of the gases listed above. For instance, hydrogen sulfide, present in eggs, may not indicate foreign gas contamination. Benzoic acid or sodium benzoate is often used as a preservative in prepared foods; it would be extracted in Section III of the Qualitative Analysis Procedure and give the test for benzyl bromide or bromobenzyl cyanide. Other interfering substances must be considered by the analyst before making a positive report.

Cleaning of Apparatus

Scrupulous attention must be paid to the cleaning of all analytical apparatus and sample containers in order to prevent the contamination of one sample from another. A paste of bleaching powder, as indicated in the sampling directions, is useful in cleaning any apparatus. Treatment with hot alcoholic potassium hydroxide destroys or removes most gases, concentrated nitric acid removes mustard gas efficiently, while rubber or

metallic apparatus may be treated by immersion in boiling water for 30 minutes. The usual dichromate-sulfuric acid cleaning solution should be used on glassware after the other decontaminating solutions are employed.

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FOOD AND POISON GASES

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In considering the possibility of contamination of foodstuffs by poison gas, it is important to bear in mind that:

(a) Poison gases are highly penetrative.

(b) Foodstuffs are often highly absorbent, particularly moist and fatty foods.

(c) Wrappings and packing materials may be absorbent and may permit the passage of poison gas.

(d) Gas can penetrate wherever air can enter (gas masks excepted)

(e) Any material which soaks up oil or water will absorb and eventually permit the passage of gas.

(f) Ventilation may be helpful, but also provides a means of entrance for the gas.

It is not necessary to discard all affected foodstuffs, however, after exposure to poison gas. Whether or not food can be salvaged depends on the type of the chemical agent, the degree of exposure, the kind of food, the manner in which it is packaged, and the way it has been protected.

All war gases contaminate food either by going into solution in the water or fat present in the food, or by being adsorbed on the solid surface. In either case chemical actions may occur which will result in some decomposition of the chemical. If hydrolysis takes place, the absorbed substance loses its original properties and, generally speaking, becomes innocuous. No such beneficial action occurs in the case of lewisite and the other arsenical gases, however; with these agents, even though the original property of the chemical is destroyed, danger of poisoning remains because of the presence of arsenic. Moreover, the action of hydrolysis is slow and therefore food may remain contaminated for a considerable period, depending on the degree of initial exposure. Many of the decomposition products resulting from hydrolysis may be unpleasant but not toxic and their only action is to render food unpalatable. A comparable action does not occur when the gas is absorbed by fat, and such food once contaminated must be considered as unfit for human use.

Poison gases may be divided into the following categories, for the purposes of our study: Non-arsenical non-persistent gases; arsenical non-persistent gases; persistent lachrymators; non-arsenical vesicant gases; arsenical vesicant gases; smokes. Of the non-persistent gases, the one most likely to be employed in modern warfare is phosgene. It is not considered a dangerous gas so far as contamination of foodstuffs is

concerned because, although absorbed to some extent - mainly in the outer layers of the food - its principal effect is on the palatability of the food. Foods contaminated by this and certain other non-persistent gases (including hydrogen cyanide) can often be rendered fit for consumption simply by airing them for a day or two. This is best done by spreading out the contaminated food so that a current of circulating air can carry away the residual gas. Much more dangerous are the persistent gases, particularly the vesicants. The latter are heavy, oily liquids, dangerous in themselves as well as in the vapors they give off. The danger lies in the fact that the bursting bomb, or the spray from an airplane, produces an immediate vapor cloud and also distributes droplets over a wide area. These droplets, particularly of mustard gas and lewisite, contaminate everything on which they fall and continue to give off harmful vapors until removed by appropriate decontamination procedures. In addition some gases, like lewisite, contain arsenic and there is therefore the additional hazard of arsenical poisoning.

(a) Non-arsenical non-persistent gases

These will not affect foods appreciably. Temporary effects will pass off after the gas cloud disperses and the food will be unharmed. Some slight deterioration may occur with prolonged exposure to a relatively high concentration of a gas of the phosgene type but it should be remembered that the palatability is more likely to be imparied than the general wholesomeness of the article of diet. The effects of phosgene on certain foods and the treatment advised are given in the following table:

Effect of Phosgene on Foods

Food	Effects	Dangerous	Treatment
Flour	Makes poor loaf, becomes sour and unpalatable	No	Air for 48 hr. Mix with 5 parts of undamaged flour to improve baking quality
Bread	Unpalatable (outer layers)	No	Air after cutting away outer layer
Cereals	Negligible	No	Air 48 hours
Meat and fish	Surface may show discoloration	No	Improved by airing and cooking
Milk	Affects taste	No	Boil
Cheese, butter, fats	Bleaches surface	No	Remove affected part which may be used for cooking
Fresh fruits	Almost none	No	Wash, air, and peel off skin and outer layer
Dried fruits	Slight loss of taste	No	Wash, air and cook

Food	Effects	Dangerous	Treatment
Fresh vegetables	Sometimes slightly bleached	No	Wash, air, and cook
Tea, coffee	Bitter	No	None is effective; blend with undamaged stock

(b) Arsenical non-persistent gases

These are usually the sternutator gases and it is considered improbable that they would significantly affect foods, since they are readily dispelled. Airing is said to be the appropriate treatment. In addition, chemical analysis should be carried out to discover any arsenic contamination which may occur on prolonged exposure in an enclosed space. If there is any possibility of contamination with arsenic, the food should not be eaten until passed on by competent experts.

(c) Persistent lachrymators

It is thought unlikely that these gases will be used on civilian populations. However, they render foods unpalatable. Airing is the only treatment that is likely to be of value, and this will prove ineffective if much gas has been absorbed.

(d) Non-arsenical vesicant gases

Gases of this class, which includes mustard gas, may prove harmful to food, particularly with prolonged exposure to high concentrations of vapor. All foods contaminated with the liquid form must be viewed with suspicion. Fatty foods (milk, cream, butter, cheese, fatty meats, eggs, etc.) contaminated either by vapor or by liquid will almost certainly be highly dangerous and should be destroyed.

Slight contamination with mustard gas vapor may affect palatability but, except for fatty foods, the materials should be edible after 48 hours' airing and cooking.

Effect of Exposure of Uncovered Foods to Low Concentration of Mustard Gas Vapor

Food	Effects	Dangerous	Treatment
All types (except fatty materials)	None except occasional slight loss of palatability	No	Airing. Discard surface layers (lean meat)
Fatty food (milk, cream, cheese, butter, margarine, fats, oils, fatty meats, fatty fish)	Rapid absorption of poison	Probably	None effective

The subjective detection of mustard gas in dry foods is rather difficult since they rarely show marked changes. Moist foods, however, will show brown spots or other surface changes. Cucumbers are particularly sensitive. In green peppers, green beans, peas, pears, gooseberries, apples, lemons and oranges the spots do not appear for 24 hours, and it takes three days for the spots to develop in beets and radishes.

Studies on the impregnation of food with mustard gas have shown that dry foods treated with 0.1 cc. of the agent remained poisonous for 20 days when kept at 12° C., and for 6-8 days at 20° C. Flour moderately contaminated may remain poisonous for 1 month at 16° C. (While in general increased temperatures are beneficial in increasing the rate of aeration and removal of vapors, heat is not always permissible or readily available.)

(e) Arsenical vesicant gases

Lewisite belongs in this class. Food which has come in contact with these gases, whether vapor or liquid, should not be eaten because of the great danger of arsenical poisoning. The salvaging of foods exposed to this gas depends on the degree of contamination and the suitability of such food for consumption should be passed on only by qualified experts after a thorough chemical examination. In case exposure has been to vapors only, it may be possible to salvage some of the food by discarding the outer layers before airing, but none of the food should be eaten until a chemical analysis shows that the concentration of arsenic is within safe limits. In case of contamination with the liquid, decontamination will probably be impossible.

(f) Smokes

Protection against solid chemicals, "smokes", is not difficult. While they penetrate all ordinary fabrics and cracks, most wrappings will be impervious to them. The clouds are easily dispersed and in still air they settle to a much greater extent on horizontal than on vertical surfaces. Prolonged airing of contaminated foods is suggested.

Protection Against Contamination With Gas

The following table summarizes the data on the protective value of various coverings for foodstuffs, given in the pamphlet issued by the British Ministry of Food:

Protective Value of Coverings for Foodstuffs

Material	Protection Against Poison or Vapor	Protection Against Liquid Poison Gas
Sealed metal	Complete	Complete
Metal, tight cover	Fairly good	Good

Material	Protection Against Poison or Vapor	Protection Against Liquid Poison Gas
Glass bottles, etc. with sealed top of similar material	Complete	Complete
Bottles, jars, etc. with grease-proof paper seals	Fairly good	Fair
Sealed wooden barrels	Complete	Complete
Waxed cartons	Good	Good
Cellophane	Good	Good
Paper cartons	Good	Fairly good
Metal foils	Good	Good
Wooden boxes	Good	Poor
Cardboard boxes	Good	Poor
Paper bags, etc.	Poor	None
Textiles, sacks, etc.	None	None

Some protection against gas is also afforded by the proper stacking of packaged goods. Closely stacked piles are not readily penetrated even by vapor; therefore if penetration does occur, the packages in the middle of such stacks will be only slightly contaminated, principally on the surface. In removing the contaminant the stack naturally should be broken down in order to permit the ready circulation of air over every item in the pile.

Wood absorbs liquid and therefore protects poorly against liquid poison gas. Increased protection against vapor is provided by lining boxes with a grease-proof paper. If such material or cellophane is unavailable, ordinary paper may be made partially gas-proof by covering the surface with paste.

Textiles generally are useless in themselves, but are valuable as screens to prevent liquid from splashing onto the piled material. They also absorb vapor and liquid and will therefore offer some protection when used as a secondary cover over an impervious inner covering of paper.

Water Supplies

The effects of the war gases on water supplies and the treatment advised are considered in the section on "Water and Chemical Warfare."

Growing Crops

Growing crops are likely to be contaminated by a chance bomb or spray intended for another objective. Scorching and bleaching of vegetation would occur in the immediate vicinity of the bomb explosion or wherever spray was liberated by low-flying aircraft. The effect, however, would be transient since exposure to weather will, in time, remove all traces of the poison and the vegetation will recover. The recovery period for non-arsenical gases is said to be about one week. Arsenical gases of the lewisite type are much more damaging because of the toxic effect of the arsenic and a much longer period will be required for the recovery of vegetation when the contamination is severe.

Foodstuffs on Farms

Special measures for the protection of food supplies on farms do not appear to be necessary. None of the modern war gases, except the arsenical gases, are likely to affect stacks of hay, unthreshed grain, or other farm stocks to an extent that cannot be remedied by airing or natural weathering. Protective coverings, tarpaulins, canvass, or sacking provide useful protection by soaking up liquid, thus reducing direct contamination.

The question of effects on livestock is a more serious matter. Animals may have to be slaughtered if they show evidences of poisoning, particularly from the persistent vesicant gases.

Warehouse Goods, etc.

Common sense in storage will prevent much damage to foods. Foods stored in cold rooms are reasonably safe from gas provided closures are fairly air-tight and precautions have been taken to prevent the entrance of contaminated air through the ventilating system.

Food in packages may be protected by covering it with oil-painted tarpaulins. Danger of serious contamination by gas splashes may also be decreased by the use of canvas or sacking covers. It is good practice to avoid storing goods in the cellar or on the top floor.

Retail Stores, Hotels, etc.

Goods should be kept in original packages as long as possible. As in warehouses, tarpaulins, canvas, or sacking covers are useful in preventing contamination from splashes of gas. Cold storage chambers should be air-tight, in order to give complete protection. Displays of goods in windows or shelves, etc. should be kept to a minimum.

Foodstuffs in the Home

Foods in air-tight containers (sealed tins and bottles) are completely protected against gas. If there is any question as to the container, it may be wrapped in cellophane as an additional protection. In order to protect the outside of containers from contamination, as many as possible should be stored in inside cupboards, wooden, or cardboard boxes.

Flour, rice, sugar, and similar non-perishable foods should be stored in tin or glass containers with tight covers, and additional protection may be provided by wrapping with cellophane or waxed paper.

Bread should be kept in tins with well-fitting lids.

Perishable foods, meat, fish, eggs, milk, and butter should be reasonably safe in the ordinary kitchen refrigerator, provided the doors and cracks have been made reasonably air-tight.

Miscellaneous

Cigarettes and other tobacco products are sources of danger in the event of the use of poison gases. The general methods used to protect foodstuffs against gas contamination will be effective with tobacco products but opened packages of cigaretts, smoking or chewing tobacco, or cigars had best be disposed of in the event of known or possible exposure to poison gas. The trivial cost of most of these materials, as well as the unlikelihood that individuals will have large supplies on their persons or in their homes, make it inadvisable to salvage the few affected items by lengthy aeration methods.

The identification of gas-contaminated meats is a rather difficult procedure. In the event of the release to the public of such meats by unscrupulous dealers, the only means of determining the degree of contamination will be by chemical methods, especially if surface stains and changes have been cut away. In case of doubt, a chemical determination for arsenic should be made, in addition to other tests, in order to make certain that any arsenic present is within permissible limits. One European authority considers solid food toxic if 100 sq. cm. of surface contain 0.05 mg. arsenic soluble in organic solvents.

Decontamination

The inexperienced individual should not attempt decontamination or salvage of food stocks. The sources of danger are many and these can be avoided only by carefully trained personnel provided with adequate decontamination equipment.

In all cases the suitability of food for consumption is a matter of expert opinion after careful examination. Food suspected of having been in contact with poison gas should not be eaten until it has been chemically tested, and salvage should be left to the proper local authorities. Whenever there is any suspicion of food contamination, this should be brought immediately to the attention of the authorities.

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MEDICAL ASPECTS OF SOME SYSTEMIC POISONS

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Toxic elements or radicals cause injury according to manner of carriage into tissues, i.e., nature of compound in which they are present, thereby establishing solubility, locus of absorption and distribution, manner of breakdown in body and mode of excretion. No necessarily uniform effect. Example: arsenic in various forms and combinations, with varied symptomatic and pathologic picture.

Arsenic

I. Common arsenic compounds

A. Arsenic trioxide - lethal dose approx. 2.7 mg As/Kg, orally

B. Mapharsen (Trivalent)

C. Tryparsamide (Pentavalent)

II. Arsine

A. Toxicity

1. Slight symptoms after several hours — 30 p.p.m.

2. Dangerous - 1 hour — 50 p.p.m.

3. Fatal - half hour — 250 p.p.m.

B. Mode of Action

1. Combination with Hb)

2. Oxidation to arsenious acid) mechanism questionable

3. Hemolysis - extensive)

4. Anemia in few hours)

5. Circulatory failure

C. Symptoms and signs

1. Vertigo, headache, nausea, vomiting, epigastric pain

2. Hemoglobinuria, hematuria, anuria

3. Jaundice

4. Circulatory failure, pulmonary edema

D. Diagnosis - History of exposure, clinical picture, quantitative analysis

E. Treatment - Supportive - transfusion?

III. Lewisite

A. Sat. Vapor at 40° C ≈ 15.6 mg/L (36% arsenic)

B. Toxicity

1. Lethal conc. in air 0.048 mg/L or 1/325 of sat. vapor at 40° C

≈ (3000 p.p.m. or)
(1000 p.p.m. As)

2. Cutaneous - 0.02 cc/sq. cm. - Total dose man 1.4 cc ≈ 0.95 g. As? (Vedder)

0.334 mg/L in form of vapor, or 21,000 p.p.m. causes vesicant action

C. Mode of Action

1. Cutaneous vesicant - mechanism?

2. Pulmonary irritant - mechanism?

3. Systemic poison (arsenic) by cutaneous absorption

D. Diagnosis - History, clinical picture, quantitative analysis

E. Treatment (Skin contact)

1. Wash off with solvent

2. Hydrolyze with NaOH or better H_2O_2

3. Excise lesions to remove arsenic (12 to 24 hours)

<u>Hydrocyanic acid and other cyanides</u>

Use of cyanides in some form anticipated, because of speed of action of CN radical - minutes to few hours, because of high toxicity, because of experimental work done over a period of years in foreign laboratories.

I. Hydrocyanic acid

A. Toxicity

HCN - fatal short exposure at 3000 p.p.m. - dangerous 150 p.p.m. - lethal dose about 50 mg

B. Mode of entry

gas HCN - inhalation and cutaneous absorption

C. Toxic mechansim

Suppresses oxidation, by paralyzing cellular oxidases in all probability (combines with iron) i.e., cellular asphyxia in presence of adequate oxygen in blood.

D. Symptoms

Initial stimulation of respiration (unimportant clinically because fleeting warmth and slight burning of skin in contact with gas (through clothing) in presence of 5000 to 8000 p.p.m. in air, (no effect in concentrations of 1600 to 2000 p.p.m. in air) with gas mask protection.

Weakness and perhaps headache

Nausea and vomiting

Dyspnoea with chest constriction

Unconsciousness

(All symptoms may be lacking in high concentrations, unconsciousness occurring in as little as 30 seconds in 6000 to 8000 p.p.m.)

E. Diagnosis

Odor of bitter almonds on breath

History of exposure

May be no cyanosis but often present after respiratory failure

Low differential O_2 content of arterial and venous blood

By exclusion of CO, respiratory irritants (no appreciable irritation of upper resp. tract), arsine (hemolysis)

P.M. diagnosis by cyanmethemoglobin (difficult)

F. Treatment

Artificial respiration in fresh air

Artificial respiration with O_2 or O_2 and CO_2 mixture

Warmth

As long as heart is beating recovery need not be despaired of

Specific treatment dependent upon two principles

1. CN converted to thiocyanate in body, and so excreted in essentially harmless form. Sulphur compounds, therefore, indicated, especially thiosulphate.

2. CN combines with methemoglobin to form relatively non-toxic compound. Therefore, Hb should be converted to met Hb, to combine with CN and diminish its toxic action. Hence use of methylene blue and nitrites and oxidizing agents $NaNO_3$ found especially effective.

Other principles have been investigated

3. Heavy metal salts like iron combine with CN to form complex, non-toxic or less toxic compounds. Unfortunately the heavy metal compounds are toxic in themselves, and therefore, sufficient dosages cannot be used without the risk of heavy metal poisoning.

The observations of Chen (Am. J. Med. Sc. 188:767, (1934)), and his associates on dogs have resulted in the use of sodium nitrite and sodium thiosulphate, giving the one after the other (never together), with amyl nitrite used when needed as a stop-gap until sodium nitrite can be prepared and given. The sodium nitrite works promptly, the thiosulphate slowly, but this is apparently a synergistic effect of the two.

Treatment advised

Pearls of amyl nitrite at first

$NaNO_2$ 0.3 to 0.5 gm in 10-15 cc H_2O

Na thiosulphate 25 gm in 50 cc H_2O administered over period of 10 to 15 minutes

Adrenalin or Coramine to support cardiac action, if needed.

Repeat half dosages of above after 2 hours or as needed for maintenance

Keep under observation 24 to 48 hours

G. Sequellae

Essentially those of asphyxial sequellae

Some tendency to persistent weakness for weeks or months

Case reports show speech defect (slow fatigued tongue) , loss of memory, inability to sustain attention

II. Other cyanide compounds

A. Toxicity

NaCN 6 mg/Kg subcutaneously in dogs (Chen et al)

B. Mode of entry

1. Salts - by ingestion in food or water

2. Organic compound - by inhalation or skin absorption

Hydrogen Sulfide and Carbon Monoxide

Mode of Action

H_2S C.N.S. poison with paralysis of resp. center. Death from asphyxia - No combination with Hb except post mortem - Green yellow color

CO - Firm union with Hb displacing O_2 with 300 times O_2 combining power

$$\% \text{ Hb CO} = \frac{P_{co} \times 300}{P_{o_2} + (P_{co} \times 300)}$$

Example: 0.07% = 50% Sat. HbCO

Symptoms: Percent saturation of blood

Headache	30
Unconsciousness	60
Early death	80

In parts/million

Toxicity	HCN	H_2S	CO	Arsine
Slight Symptoms after several hours	20-40	100-150	300-400	30
Maximum allowable for 1 hour	50-60	200-300	400-500	
Dangerous 30-60 min.	120-150	500-700		50
Fatal in few minutes to half hour	3000	1000-3000		250
Loss of smell		100		
Lethal dose for man absorbed	50 mg			

GENERAL TOXICOLOGY OF WAR GASES

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I. Certain general considerations

Classification based at present on main effects, as for example, pulmonary irritation or cutaneous vesicant action.

Tendency to think of these in terms of physical properties, with gases as pulmonary irritants, and liquids as vesicants.

This tendency to be avoided as a generalization, since it may well be found to be erroneous in case of new war gases.

Better to think in terms of the general methods of inducing exposure and the effects that are sought for in the use of war gases. The former is concerned with the mode of attack on the human organism i.e. avenues of entry. The latter has to do with the means by which noxious substances interfere with physiological mechanisms.

Present discussion aims to give practical information on the chemical agents now known to be available, as a means of providing protection against these specific substances, but it also uses them to illustrate certain general principles that may serve as guides in avoiding the worst consequences of new agents.

II. Physiological considerations

A. Mode of absorption or injurious contact - in order of decreasing practical importance

1. Inhalation

a. Effect may be irritation (local injury) and/or general toxic effect.

b. Matter of volatility or fine state of subdivision in air breathed through nasal, pharyngeal and bronchial passages.

c. Degree of volatility in physical sense not so important as relative toxicity of vapor, e.g., mustard gas with vapor pressure of only 0.065 mm, Hg at 20° and volatility of only 0.625 mg/L is highly dangerous, since a concentration of 0.15/L may produce death if inhaled for 10 minutes or longer. Likewise, Lewisite has a vapor pressure of only 0.395 mm Hg at 20°, and a volatility of 4.50 mg/L, while the lethal concentration for 10 minutes of inhalation is only 0.12 mg/L. The saturated vapor of these materials at ordinary temperatures must be diluted 4 times and 37 times respectively, if fatal effects are to be avoided from even brief exposure.

Note: Neither these nor many other toxic vapors can be detected by their odor to such an extent as to provide safety. They do not give adequate warning of their presence, and many others give no warning at all. An odor or a sensation of stinging or burning of eyes, skin, or nasal mucosa must be taken as a sharp warning.

2. Skin contact

a. Effect may be local injury, and/or general toxic effect. Local injury due to corrosive or burning action - immediate or delayed.

Local injury due to absorption into skin with subsequent breakdown of compound, releasing poisonous radicals. General intoxication from absorption of compound.

b. Non-persistent gases absorbed thru skin only in high concentration - skin absorption implies a liquid material, with relatively low volatility of a fat soluble type.

c. Except in case of immediately irritating substances that give their own warning, skin injury or absorption is relatively slow and materials can be removed without injury if done quickly and thoroughly, i.e, within 5 to 30 minutes dependent upon the compound and the size of the dose required to produce injury.

Note: There may be no warning of any kind, other than that of noting the presence of some foreign material on the skin or clothing, or on objects in the environment. Dependence cannot be put upon the existence of an odor or an irritating effect upon the eyes or nose. The latter, if present, will be helpful.

3. Ingestion (Swallowing)

a. Poisonous materials taken into the gastroenteric tract may be decomposed by water, food, or the digestive juices into harmless materials, or into others equally or less toxic compounds.

There may be no chemical change, in which case, the poisonous materials may produce local effects like those on the skin or lungs, or they may be absorbed with such general or specific effects as are characteristic of the compound, or they may be evacuated from the alimentary tract without injury or illness.

b. In general the lethal dose of a material taken by mouth is considerably greater than if it is inhaled or injected intravenously. It is usually less than if it had been applied on the skin. In the case of oil-soluble components the lethal dose by mouth may be four to ten times the lethal dose by inhalation, and if the material is irritating, it may be evacuated promptly, thereby preventing more than slight absorption.

Note: Warning is usually given against inadvertent ingestion of food contaminated with chemicals of the type employed as war gases, by reason of a foreign taste. Food or water that has had an opportunity for contamination should not be eaten if it has any foreign taste, unless expert examination indicates that it is safe for use.

B. Types of injurious effects - in decreasing order of toxicologic importance.

1. Systemic poisons - alkaloids, heavy metals and metaloids, narcotics, catalytic poisons and asphyxiants

a. None available for practical use at present with possible exception of arsenic compounds.

b. Entrance into body may be by any route.

2. Production of injury to lungs.

a. Immediate effects (acute irritation).

b. Delayed injury - (without warning).

c. Permanent injury - (complications, scarring).

3. Production of injury to skin

a. Immediately painful injury - (acute irritation),

b. Delayed insidious injury with disability.

c. Permanent injury - (infection, scarring).

4. Production of acute irritation of eyes or nasal mucosa, respiratory tract, or gastroenteric tract, with temporary acute disability, as nuisance in itself, or as means of breaking down protective measures (compelling removal of gas masks, etc.).

5. Combination of two or more of above effects in same compound or in mixtures of compounds.

III. <u>Specific effects of certain presently available agents</u>

A. Pulmonary injurants - in decreasing order of toxicity

1. Phosgene and diphosgene

a. Characteristic odor but little irritant effect and, therefore, little warning, except in high concentration.

b. Relatively little effect upon upper respiratory tract and eyes, therefore, little in way of upper respiratory symptoms, except from quite high concentrations.

c. Injury to lung tissue mainly, with pulmonary edema after short or long latent period. Chest constriction, cough, blood-streaked sputum, becoming later pink and frothy, with increasing amounts of fluid.

d. Little difficulty from contaminated food. Bad taste.

Warning. Insidious. All casualties to lie down as soon as possible, to be carried on a stretcher and put to bed at complete rest at earliest possible moment after exposure.

2. Chloropicrin

a. Characteristic odor and irritant effect upon eyes and nose, therefore, sharp warning.

b. Symptoms are those of upper respiratory irritation and discomfort, lung irritant with cough constricting pain, blood-streak sputum, and general lung damage of a severity depending upon concentration to which one is exposed.

c. Gastro-enteric symptoms, nausea, vomiting, abdominal pain and diarrhoea from swallowing material in foods or in secretions from upper respiratory tract.

d. Burning, stinging of eyes and weeping.

Warning. Used to produce intolerable burning of eyes and vomiting so as to cause removal of gas mask and induce exposure to more toxic gases (phosgene, etc.) with which it is mixed. Masks must be kept on.

3. Chlorine

a. Immediate irritant effect upon eyes and upper respiratory tract, therefore adequate warning. (Not so irritant to eyes as chloropicrin).

b. Extensive acute upper respiratory irritation and injury, hoarseness and loss of voice, sore throat, with cough, chest pain, and constriction, and often delayed pulmonary edema.

c. Most important effect is injury to lung, with general edema of lung and danger of asphyxia.

d. Little or no trouble from contaminated food. May be strong taste.

Warning. All but the lightest cases of exposure are in danger of developing pulmonary edema, and all casualties should lie down and be transported, and kept in bed for not less than twenty-four hours of observation.

B. Vesicants

1. Mustard

   a. Primary injurious effect on skin, latent period of some hours, after which redness, followed by blistering, develops.

   b. Serious injury to eyes from droplets, with latent period before damage shows up.

   c. Acute injury to nose, throat, larynx and lungs from inhalation of vapor, some time after breathing, with sore throat, cough, loss of voice, pain on talking, chest pain, bloody sputum, and hemorrhage from nose, throat, or lungs.

   d. Salivation, upper abdominal pain, nausea, vomiting, watery, bloody or tarry diarrhoea, weakness, emaciation, beginning from 1 to 12 hours after swallowing contaminated food or other material.

   Warning. There is little or no immediate irritation of the skin, eyes, nose and throat or chest, and, therefore, no recognition of danger. Immediate decontamination is necessary to prevent disabling injury if material comes in contact with skin or clothing. Prompt use of mask and continuous use until liquid and vapor is disposed of is absolutely necessary.

   There is likely to be little recognizable taste or other objectionable quality to food. Great care necessary, therefore. Suspected food must be discarded or subjected to rigid chemical examination before use.

2. Lewisite

   a. Primary injurious effect on skin, with short latent period and perhaps early stinging and redness of skin, followed by blistering and ulceration.

   b. Serious injury to eyes from droplets, with short latent period.

   c. Acute injury to nose, throat, larynx, and lungs from inhalation, beginning shortly after exposure and developing in severity, with sore throat, cough, loss of voice, pain in chest, prostration.

   d. Abdominal pain, nausea, vomiting, with watery, bloody, or tarry diarrhoea, with also weakness and emaciation, the first symptoms occurring within an hour or less after ingestion of contaminated food or other material.

      Symptoms of acute or sub-acute arsenic poisioning may result if one survives the initial acute toxic effect of the whole molecule, i.e. gastro-enteric ulceration, jaundice, bronchitis, paralyses of legs and/or arms, scaling skin lesions, loss of hair and nails, etc.

<u>Warning.</u> There may be little warning of the presence of Lewisite in the atmosphere. The compound used may be entirely odorless. The presence of droplets of material on objects may be noted. Prompt use of the mask, and immediate decontamination of skin is necessary to avoid disabling injury.

Food in the involved area must be regarded as unfit for use, unless completely protected. Questionably contaminated food must be discarded, unless shown to be safe after chemical examination.

IV. Toxicity data for certain agents

Toxicity of Vapors Inhaled

In Milligrams per Liter of Air

	Phosgene	Chloropicrin	Chlorine	Mustard	Lewisite	Ethyldichlorarsine
Sat. Vapor Conc. 20° C	Gas	165	Gas	0.57	4.50	47.0
Fatal 30 min.	0.36	0.8	2.5	0.07	0.05	0.80
Fatal 10 min.	0.50	2.0	5.6	0.15	0.12	0.50

Toxicity of Vapors in Contact with Skin

In Milligrams per Liter of Air

	Mustard	Lewisite
Sat. Vapor Conc. 20° C	0.625	4.50
Vesicant concentration	0.005	0.33

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Toxicity of Liquid in Contact with Skin

	Mustard	Lewisite
Speed of absorption	20-30 min.	5 min.
Latent Period of First Effect	120 min.	30 min.
Lethal Dose for man	?	2.6 grams

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Roughly Estimated* Lethal Dose when Swallowed

Agent	Lethal Dose for Man*
Phosgene	-
Chlorine	-
Chloropicrin	1200 to 2400 mg
Mustard	60 to 120 mg
Lewisite	70 to 150 mg
Ethyldichlorarsine	300 to 600 mg

* Not to be taken as correct. Calculated indirectly from the lethal concentration for inhalation. Experimental data not available.

SUBJECT: OUTLINE OF THE PREVENTION AND FIRST AID TREATMENT OF CHEMICAL CASUALTIES.

Leon Goldman, M.D.

GENERAL REMARKS: A knowledge of the chemical warfare agents will not only do much to dispell the fear and panic inspired by them, but also this knowledge will serve to show how relatively simple the outlines on both prevention and the very important first aid measures are.

I. Prevention - by planning to avoid contact with the chemical warfare agents

A - Personnel not required to be on streets

1. Inside - doors and windows closed

2. Ascending to higher floors

3. Gas protection shelters as available

4. Try to evacuate in advance, old people, invalids, and children

B - Personnel authorized to be on streets

1. Gas mask

2. Protective clothing - type depending upon duties

3. If situation warrants - a station much above street level

II. Prevention - during and immediately after a chemical warfare attack

A - Personnel not required to be on streets

1. Direction of movement - up wind; right angle to the gas cloud

2. Go inside house; close doors and windows tightly - turn off air conditioning - ascend to higher levels - avoid remaining in low, poorly ventilated areas, basements, etc.

3. Improvised gas masks - wet handerchief or cheese-cloth with water or baking soda solution

4. Improvised protective clothing - rain coat, collar up, sleeves down; heavy clothing; cover head to prevent contamination of scalp and hair

5. For vesicant contamination of clothes - discard as rapidly as possible or go in doors and put clothes in metal container - (ash can or garbage can)

Persons with contaminated clothing should not be permitted in any public shelter. Bathing and use of any active chlorine compound (or hydrogen peroxide for lewisite) or baking soda paste if these other materials are not available.

6. For vesicant contamination of the skin do as much of the approved skin cleansing technic as possible after discarding the contaminated clothes. To remove the agents, use soap and water. After mechanical removal, use prophylactic agents if available. Contamination by liquid vesicants is a definite medical emergency! A shower with hot water and soap after initial decontamination finished is always necessary.

7. Vesicant contamination of eye is a definite medical emergency! Irrigate with water or baking soda solution or put face in pan of water. Medical attention should be obtained as soon as possible.

8. Vesicant contamination of hair. Wash with soap and water and any active chlorine compound available. If lewisite, use hydrogen peroxide; cut hair off quickly if contaminated by liquid.

B. Civilians authorized and required to be on streets

1. Put on gas mask in the approved fashion.

2. Use protective clothing or protective covering as indicated.

3. If contaminated - proceed according to instructions previously given.

III. Treatment

A. Irritants of the respiratory tract

1. Sternutator or sneeze gas type - there may be delay in onset of symptoms

a. Remove to fresh air

b. Smell chlorine from bottle containing bleaching powder.

c. Sodium bicarbonate gargle and mouth wash and if necessary nasal irrigation, then spray with neosynephrin and pontocaine if available.

2. Pulmonary irritation - phosgene group - every individual not wearing a mask exposed to "heavy" concentrations of phosgene must be considered as potential casualty or may be actual casualty. Remember the onset of symptoms may be very insidious! At times, dislike of cigarette smoking or smoke may be indicative of pulmonary irritation. The exposed persons may pass successfully

through the stages a, b, and c below. The final stage reached will depend upon the severity of the exposure.

a. The mild case - good color, no difficulty in breathing, etc.

(1) Rest, heat, drinks (coffee or tea)

(2) Stretcher evacuation

(3) Observation in hospital for appropriate period

b. The moderate case - chest pain, slight cough, etc.

(1) Rest, heat, drinks (coffee or tea)

(2) Should have priority in evacuation over "a"

(3) Treatment in hospital necessary - oxygen if available.

c. The severe case - cyanosis blue or gray (shock) type, pulmonary edema.

(1) Same emergency treatment as above

(2) Immediate evacuation to hospital

(3) Hospital and not casualty station treatment

(4) Oxygen, sedation, plasma, venesection if increased venous pressure.

(5) Long period of observation and later observation of response to effort.

B. Treatment of the lesions from vesicants - all personnel treating casualties contaminated with vesicants must be protected themselves with gas masks and some form of protective clothing. There is a great difference in lesions from vapor and from liquid contact.

1. Eye lesions - profuse irrigation with plain water or 2% soda bicarbonate, in the approved fashion avoiding all pressure on eye. Do not use any of the strong agents recommended for decontamination of the skin! After irrigation may instill ophthalmic ointment of various types:

a. Bland

b. "Sulfa" ointment

c. 2% Sodium bicarbonate

d. No cocaine, if local anaesthetic needed in the eye, use butyn or pontocaine. Do not bandage the eyes! If lesion develops it is much better to secure immediate consultation from an ophthalmologist. For any burns of the skin around the eye, treatment of bland therapy should be done but do not allow bandage to come over the eye. Remember eye burns may develop insidiously also.

2. Treatment of the skin area contaminated with vesicant before appearance of lesion - ideal period for lewisite five minutes and for mustard maximum one-half hour. Questionable whether protective treatment of any value with pure vapor contamination (?)

a. Removal of contaminated clothing but continued wearing of gas mask until main sources of contamination are removed.

b. Determining the approximate area of cutaneous contamination, the approved method of cleansing technic (see above) followed by prophylactic materials such as protective cream of the Chemical Warfare Service, bleaching paste mixtures, Chlorox, sodium hypochlorite, dichloramine, azochloramide. For lewisite, hydrogen peroxide preferred to those chlorine compounds. Baking soda pastes may be used if none of the above are available. If none of these materials are available rinse with water, since no time should be lost. If possible take a shower using plenty of hot water and laundry soap.

3. Treatment of the actual skin lesions from vesicants - Do not use any medications recommended for prophylactic use when this phase develops. The treatment of the blister stage should be done by medical personnel. Do not break the blisters. Do not cover the blisters with greasy ointments. Avoid getting the skin dirty. The skin may be covered with clean, dry bandages.

C - Treatment of Lesions from Cyanides

1. Artificial respiration as soon as possible -
Use portable pulmotor apparatus if available

2. Inhalation of amyl nitrite

D - Treatment of burns from Incendiaries and the like

1. Phosphorus Burns - specific emergency treatment important, cover immediately with 2% copper sulphate solution, if none available cover with oil or warm water or 5% soda bicarbonate solution until phosphorous particles can be removed. Instead of baking soda the following alkaline paste may be used

Magnesium oxide (heavy)	10%
Borax	5%
Soda bicarbonate	85% (Godding and Notton)

Instead of the 2% copper sulphate solution the following copper paste may be used:

Copper sulphate	22.5%
Glycerine	67.5%
Starch	5.0%
Water	5.0%

2. Heat Burns

A. Extensive - use no greases, tannic acid jellies or the like; cover burns with clean bandages; do not get dirty; keep patient warm; arrange for immediate transportation to medical installation.

B. Mild - use only simple ointments here. Cover with clean bandages and protect from dirt

THE CHEMISTRY AND METHODS OF DECONTAMINATION

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Introduction

The number of chemical agents which have been used in war is relatively small considering the vast field of organic compounds that have toxic effects on man. The important factors contributing to selection of practical chemical warfare agents are the physical and chemical properties of the agent and its availability in large quantities. At present, there are twenty to thirty chemical compounds which could be used in offensive and defensive warfare. In war on civilians, however, only a few of these compounds would be of value, either for their demoralizing effect or for impairment of manufacturing facilities. Non-persistent gases such as phosgene and chloropicrin could not be maintained in sufficient concentration in large enough areas to be practical. Tear gases and sternutators are not sufficiently toxic and incapacitating. Certainly, from a practical standpoint, the vesicants, such as mustard, lewisite, and the nitrogen mustards, should be the chemical agents of choice for attack on a civilian populace. Their persistence and toxicity in low concentrations are arguments in their favor.

Of the several possible methods of dissemination of the chemical agent, only two will be mentioned. The material can be dropped from the air by bomb or sprayed from a low-flying airplane. In attempting to obtain an effective concentration of gas or liquid over a moderately large area, it would seem that spraying or sprinkling would be the most effective method, while for a maximum effect in a relatively small area, bombing could probably be employed. According to the method used, gassed areas may consist of small or medium-sized areas of heavy contamination caused by a bomb, or fairly large areas of moderate to light contamination due to sprinkling or spraying of the gas. A further distinction, that between vapor contamination and liquid contamination, must also be noted. In the case of vapor, in most instances, decontamination is accomplished simply by aeration. However, contamination by liquid requires more strenuous measures, since aeration alone causes only a slow destruction of vesicant agents, particularly mustard gas.

Of the vesicant gases recognized as practical chemical warfare agents, mustard gas and lewisite are the best known, most effective, and most easily available. Both of these materials are classed as persistent gases and are very active vesicants. Their vapors are extremely irritating to the lungs in low concentrations. Ethyldichlorarsine is another vesicant which might be employed although it is generally regarded as a non-persistent gas. The recent disclosure that the nitrogen mustards are effective vesicants brings a new problem to the decontamination personnel. However, the present methods of decontamination are general rather than specific and are applicable to these materials in most instances.

Chemistry of Decontamination

In order to understand the reactions involved in decontamination, some knowledge of the physical and chemical properties of the gases likely to be employed is necessary. If the use of non-persistent gases, tear gases, and irritant smokes is ruled out on the basis of impracticability, then a discussion of the properties and reactions of mustard gas and lewisite is sufficient for the present purpose. All the chemical agents which closely resemble either of these two materials in chemical structure will show the same chemical reactions even though they may differ appreciably in their physical and toxic properties. Very little can be said about the nitrogen mustards since their formulas are secret.

Mustard gas, 2,2'-dichloroethyl sulfide, is a liquid boiling at 217.5°. It is slightly soluble in water and readily soluble in most organic solvents. It is stable to air and only slowly hydrolyzed by water or water vapor at ordinary temperatures. At higher temperatures, i.e., 100°, it is rapidly hydrolyzed according to the following equation.

$$(ClCH_2CH_2)_2S + 2H_2O \longrightarrow (HOCH_2CH_2)_2S + 2HCl$$

The compound, hydroxyethyl sulfide, is non-toxic. Mustard reacts readily with oxidizing agents such as H_2O_2, $KMnO_4$, $K_2Cr_2O_7$ and HNO_3 with the formation of a sulfoxide or sulfone, depending upon the conditions employed.

$$(ClCH_2CH_2)_2S + [O] \longrightarrow (ClCH_2CH_2)_2S = O$$

$$(ClCH_2CH_2)_2S + [O] \longrightarrow (ClCH_2CH_2)_2S \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$$

Dichloroethyl sulfone has been reported to have vesicant action on the skin and therefore oxidation is not a completely satisfactory method of decontamination.

Mustard as a liquid reacts violently with dry chloride of lime with the formation of numerous products, but when a slurry of bleaching powder is used, dichloroethyl sulfoxide is formed.

$$(ClCH_2CH_2)_2S + CaOCl_2 \longrightarrow (ClCH_2CH_2)_2S = O + CaCl_2$$

Dichloroethyl sulfide reacts with chloramine-T forming a non-toxic sulfilimine compound.

$$(ClCH_2CH_2)_2S + CH_3C_6H_4SO_2N\begin{smallmatrix} \nearrow Na \\ \searrow Cl \end{smallmatrix} \longrightarrow CH_3C_6H_4SO_2N = S(CH_2CH_2Cl)_2 + NaCl$$

Another reaction of dichloroethyl sulfide which may be used as the basis of a decontamination procedure is that with sodium sulfide.

$$Cl(CH_2CH_2)_2S + Na_2S \longrightarrow S(CH_2CH_2)_2S + 2NaCl$$

The product formed, diethylene disulfide or dithiane, is non-toxic.

The reactions of lewisite with the reactants mentioned above are not as well worked out and in certain instances the final products are not known. Furthermore, although the term "lewisite" is applied to β-chlorovinyldichloroarsine, di(β-chlorvinyl) chloroarsine and tri (β-chlorovinyl) arsine are also present in the material which is used as a chemical warfare agent. The last mentioned compound has no vesicant or irritant properties.

β-chlorovinyldichloroarsine is readily hydrolyzed by water and is broken down rapidly in a damp atmosphere.

$$ClCH = CHAsCl_2 + H_2O \longrightarrow ClCH = CHAs = O + 2HCl$$

The product β-chlorovinylarsenious oxide is toxic because of its arsenic group and on contact acts as a vesicant.

Alkalies completely destroy β-chlorovinyldichloroarsine with the formation of acetylene and sodium arsenite.

$$ClCH = CHAsCl_2 + 6NaOH \longrightarrow C_2H_2 + Na_3AsO_3 + 3NaCl + 3H_2O$$

Oxidizing agents such as nitric acid and hydrogen peroxide react readily with β-chlorovinyldichloroarsine, forming β-chlorovinylarsenic acid.

$$ClCH = CHAsCl_2 + [O] + 2H_2O \longrightarrow ClCH = CHAs(OH)_2{=}O + 2HCl$$

β-chlorovinyl arsenic acid formed, on treatment with warm concentrated sodium hydroxide gives sodium arsenate and acetylene.

$$ClCH = CHAs(OH)_2{=}O + 4NaOH \longrightarrow Na_3AsO_4 + C_2H_2 + NaCl + 3H_2O$$

β-chlorovinyldichloroarsine reacts readily with chloride of lime, but the reaction has not been studied and the products formed have not been reported. It is reasonable to assume that oxidation and hydrolysis are the first steps.

$$ClCH = CHAsCl_2 + CaOCl_2 + H_2O \longrightarrow ClCH = CHAsO_3H_2 + CaCl_2$$

General Decontamination Procedures

The reactions given above form the basis of most of the decontamination procedures in use at present. The general effectiveness of chloride of lime and its cheapness make it the agent of choice for chemical destruction of the vesicant gases on sites and articles when the effect of the decontamination agent is not a deterent. In many instances, however, other decontaminating agents or procedures must be used in order to avoid harm to the material being decontaminated. An outline of the possible methods of decontamination is given below.

Decontamination

- Removal
  - Hosing
  - Solvent
  - Mopping
- Destruction
  - Burning
  - Boiling
  - Chemical Agents
- Sealing
  - Earth and Sand
  - Sodium Silicate
- Weathering
  - Sun
  - Wind
  - Rain

Under weathering is found the effect of the sun, wind, and rain. The heat of the sun will cause vaporization of the liquid material from contaminated surfaces and dilution with air dissipates the toxic vapor with the aid of wind. Rain and moisture will rapidly decompose lewisite, but mustard is only slowly affected. However, a contaminated area can be marked off as dangerous and decontamination will proceed naturally until after several weeks all of the gas in the area will have been vaporized or decomposed by moisture.

Sealing is another general method of decontamination. This is generally used as a temporary measure when it is desirable to keep a contaminated area in use. Earth and sand can be used for ground areas, paths, and dirt roads. Brick work, concrete, and plaster contaminated with liquid vesicants can be treated with sodium silicate solution which will seal in the liquid and prevent its vaporization. This is a method of expediency and should not be used except in cases requiring a quick occupancy of the contaminated building.

The third method of decontamination which can be employed is removal with an organic solvent or with water. Streets and concrete surfaces can be vigorously hosed to wash off liquid vesicants. In the case of lewisite this will also decompose the chemical agent and wash off the product of hydrolysis. Any dichloroethyl sulfide removed in this manner, however, will collect in the bottom of the drains and in the bottom of pools near the building or area treated and evaporation of the water will permit this material to vaporize, causing a fresh contamination. Mopping can be used for floors not equipped with drains but it is not particularly recommended.

Metal objects which would be corroded by the use of bleaching powder can be wiped with rags wetted with kerosene or gasoline to dissolve the contaminant. The thin film of vesicant and solvent remaining can be removed by repeating the process several times. Solvent removal of the contaminant is satisfactory when care is used in the handling of the rags containing the dissolved vesicant. Frequently this method is used to remove the gross contamination, then a bleaching powder slurry is employed, and this is followed by oil to prevent rusting.

The most important of the general decontamination procedures is destruction of the contaminant by chemical means. This is the preferred method and is used unless the character of the contaminated item prevents its use. It has been previously mentioned that chloride of lime is generally effective in destroying chemical agents. This is used in a

mixture with water to form a slurry or is mixed with earth and sand. Several other substances containing active chlorine can be used when the contaminated articles would be destroyed or harmed by bleaching powder. These are chloramine-T, Clorox, and HTH, which in dilute solutions do not have the corrosive action of bleaching powder. Sodium sulfide can be used for machinery and vehicles. Although there is no report on its effectiveness in destroying lewisite, it should react with this agent. The reaction of sodium sulfide with dichloroethyl disulfide has been given above. Alkalies such as lye and washing soda in solution can also be used effectively to destroy lewisite.

Burning is another chemical process for decontamination. Wooden parts badly soaked with mustard and lewisite can be removed and burned, and clothing and furniture if grossly contaminated should also be destroyed by burning. Care must be exercised in burning such materials, however, as there is danger of producing a toxic concentration of the vapors in the surrounding atmosphere.

Boiling or steaming is effective in destroying both mustard and lewisite and can be applied to clothing and many small metal articles. When clothing is steamed to remove lewisite, the product formed is still a vesicant and must be removed by treatment with an active chlorine compound or dilute alkali.

Nitrogen mustards are also decomposed by water, slowly at room temperature, more rapidly at higher temperatures. It may, therefore, be presumed that decontamination by boiling or steaming would be effective in the decontamination of articles contaminated with these vesicants.

In the material presented here no attempt has been made to provide specific methods which could be used in decontamination of all items that might become contaminated during a gas attack. All that has been attempted was to explain the chemistry involved in the decontamination procedures in use at present, and to outline these procedures in a general way so that they can be adapted to specific problems as they arise.

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DECONTAMINATION PROCEDURES

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The work of the decontamination squads is logically subdivided into the objects to be decontaminated such as streets, buildings, clothing, etc. First, however, let us consider briefly the personnel of the squads.

Personnel

Obviously individuals making up the decontamination squads must be trained and must be fully protected by special clothing, shoes, gloves, and gas mask. They should be inspected before commencing operations to insure that they are properly protected. Facilities should be provided for undressing and bathing after completion of their work, and the men should be taught to assist each other in removing protective clothing without allowing it to touch the bare skin. Facilities for disposal or cleaning of contaminated clothing should be provided.

Decontamination Materials

The materials most likely to be available for decontamination are:

Earth (including sand, ashes, soot, and sawdust)

Water

Chloride of lime

Other suitable but less effective materials are:

Sodium sulfide, 1% solution in water

"Green solution," 1 lb. sodium bicarbonate dissolved in 1 gallon sodium hypochlorite solution

Materials for use in special cases are:

Kerosene (gasoline)

Aqua ammonia

Chloramine T

Decontamination Equipment

The recommended supply of equipment for a decontamination squad or civilian decontamination center consists of:

20 cans (50 lb. each) chloride of lime

1 gallon lubricating oil, medium

2 cans (5 gal. each) kerosene

4 brushes, white wash (long handled)

4 decontaminating apparatus, 3 gallon (pressure type) complete with paddle and funnel, M2

1 box (12 tubes) impregnite, shoe, M1

10 yards cheesecloth, medium 2 feet wide

6 shovels (long handled)

4 rakes

4 brushes, scrubbing

4 picks or pick mattocks

4 scythes or sickles

4 brooms, stable

8 brooms, common

8 buckets, G.I., 14 quart

1 can, galvanized, 15 gallon

1 axe, single bit

20 lb. rags, clean

24 signs, "Danger -- Gas"

2 hoses, garden, 50 foot lengths

25 lb. soap, issue

4 oilers, with spout, ½ pint

4 lanterns, kerosene

6 flashlights

1 screw driver, 6 inches

4 curtains, gas-proof

In addition each squad should carry a first-aid kit consisting of:

$\frac{1}{2}$ lb. sodium bicarbonate

3 lb. soap, issue

$\frac{1}{2}$ gallon kerosene

4 oz. hydrogen peroxide -- 3% solution

$\frac{1}{2}$ pint high test bleach powder (mix in glass jar one part bleaching powder with one or two parts water)

1 teaspoon

3 medicine droppers in sterile gauze (for use as applicators)

3 oz. 2% sodium bicarbonate solution in water

Bleaching Powder

The most useful neutralizing agent for both mustard and lewisite is bleaching powder, otherwise known as chloride of lime. This material is a white powder, not very stable, which readily gives up its chlorine when exposed to the air or moisture. Chlorine reacts with mustard to destroy it, but must be brought into intimate contact with the gas.

Bleaching powder should be kept in air-tight containers until the moment of its use. Dry bleach should not be placed directly upon liquid mustard gas because the chemical reaction which takes place results in the evolution of heat and flame. This drives off a high concentration of mustard vapor which may be carried some distance by the wind, endangering people who would otherwise be safe. In using bleach on mustard gas, the bleach is either mixed with water as a paste or mixed with sand or earth.

The use of bleach is affected by the percentage of available chlorine, which varies in the different types of bleach. Chloride of lime when freshly packed may have as much as 35% available chlorine. Bleach with less than 15% available chlorine should not be used except when none better is available. There are commercial compounds, under such name as H.T.H. and Perchloron, which contain as much as 70% available chlorine. Also available are commercial bleaching solutions such as Clorox and Zonite which contain from 5 to 15% of available chlorine.

In using a compound which varies from the standard of 30 to 35% available chlorine, it is a safe rule to combine with one part of bleach, one part of inert material for each 10% of available chlorine. Thus, with one pound of 70% H.T.H. or Perchloron, 7 pounds of earth may be used; with one pound of 30% commercial chloride of lime, three pounds of earth; and with one pound of 10% chlorine, one pound of earth.

Slurry

Slurry is a 50-50 mixture of commercial 30% chloride of lime and water. This proportion is obtained by mixing two gallons of water weighing

16 pounds with three shovelfuls of bleach weighing about 16 pounds. With H.T.H. or Perchloron, one-half the amount (8 pounds) is mixed with two gallons of water. Thorough mixing to remove lumps is essential. First add about two quarts of water to the 16 pounds of bleach and work into a smooth paste; then add remaining water and stir thoroughly.

Since one square yard of area requires one pound of chloride of lime for decontamination, the above amount, which fills a three gallon sprayer, will properly treat 16 to 20 square yards.

The slurry is very corrosive to most metals and cotton fabrics. Therefore, it should never be used where this corrosive action will cause excessive damage to material and equipment. Other less corrosive agents such as one per cent sodium sulfide, "Green Solution," chloramine T, or kerosene should be substituted.

The mixing of slurry is not dangerous enough to necessitate wearing protective clothing, but this mixing is normally done at or near the contaminated area. Consequently protective clothing is usually worn.

Since chloride of lime is very corrosive, it must be completely removed from the decontaminating equipment after use. To remove all traces, all spray apparatus, mixing buckets, brooms, and other pieces of equipment are washed in several changes of water. Hot soapy water will aid in the cleaning and a plentiful supply of strong laundry soap is an invaluable item in the supply list of a decontamination squad.

Decontamination of Ground Areas

The decontamination squad, even though fully protected with special clothing, should avoid all unnecessary contact with the liquid agent or vapor. The squad should approach a bomb crater from the upwind side and commence spreading the neutralizing material at the edge of the contaminated area. In the crater, the bleach mixture or whatever neutralizing substance is used should be spaded into the soil to insure close contact with the gas.

Pools of liquid mustard or lewisite or large visible splashes on ground or vegetation are rarely found. In most cases the mustard is only perceptible by its odor. The contamination is generally greatest in the bomb crater itself, while the area outside the crater is usually much more lightly contaminated. If this area contains high grass or brush which cannot be decontaminated as it stands, it should be cut down so that it can be treated and disposed of. Neutralizing materials should be most liberally applied to spots which are the most heavily contaminated. After the entire area is so treated it should be covered with a layer of fresh earth. All these facts should be borne in mind by the decontaminating detail.

Decontaminating Streets and Roads

Whether degassing work is practicable in the case of a contaminated stretch of road will depend upon the size of the affected area, the means available, and the necessity for the work. Where drainage is assured, a contaminated hard-surfaced road may be rendered less dangerous by wetting

it down with water; much of the contaminant, if it is mustard, will be carried off in sewers and drainage ditches. Mustard gas will be decomposed very slowly by this means. The liquid mustard will sink to the bottom of pools and ditches and remain there in active form for a long time though the water seal will lessen the amount of mustard vapor given off. Consequently such a procedure is more applicable to roads and streets in cities and towns where ample drainage facilities exist. In any case, care should be taken that such measures do not merely result in spreading the contamination.

In the case of lewisite contamination of streets or roads, water will hydrolyse the gas but power flushing is needed to wash off solid hydrolyzate, which is insoluble in water but is a contact vesicant.

When time is limited, contaminated patches of paved road which cannot be avoided may simply be covered with a layer of earth to render them comparatively safe for immediate passage over them. When time and facilities are afforded, contaminated patches of paved road should be covered with bleach paste and swabbed with it. A strong solution of bleach and water might be used. The bleach should be allowed to stand for 24 hours if possible and then washed off with water. Dirt roads may be treated with bleach mixed with sand or earth.

When available, a tank truck with two spraying nozzles may be used on streets. Two men fully protected, as is the driver, ride on the front fenders and spray a 50-50 mixture of chloride of lime and water in advance of the truck.

One tank load of slurry (1,600 lb. of chloride of lime and 200 gal. of water) can cover a gravel road 8 yards wide for a distance of 200 yards. Since mustard and lewisite will not penetrate concrete or other smooth surface roads as rapidly as it does gravel, dirt, and cinder road surfaces, a larger area of the former (8 yards wide and 400 yards long) can be decontaminated.

If lewisite has been sprayed on a road it may be destroyed by hosing it down with water. A high pressure hose is preferable, though the modern street flushing truck may be used for this task. The resultant product may be an arsenic compound which is poisonous and must be washed away.

If lewisite and mustard are mixed, the normal slurry load in the power driven apparatus will destroy both vesicants.

Decontamination of Buildings

Buildings may become contaminated through direct hits by gas bombs, by the spraying or sprinkling of chemical agents from airplanes, by toxic vapors blown from nearby areas, or by the entrance of persons wearing contaminated clothing.

A grossly contaminated structure should be disposed of by burning if this can be done with safety. If it is so isolated that it will not become a source of danger because of the vapor escaping from it, the building may simply be opened and marked with a danger sign. If it is not so isolated, the building should be closed up tight (windows boarded up, etc)

and abandoned after a warning sign has been posted. If essential, because of the importance of the building and/or its dangerous location as a source of contamination, or because of the impossibility of sealing the doors and windows, decontamination operations should be conducted.

Buildings contaminated by vapor only can be cleaned by opening all windows and doors and allowing fresh air to circulate freely through them. In warm bright weather, the sunlight and wind will soon eradicate the vapor. If ventilation is poor or if the weather is cool and cloudy, the mustard vapor may persist for a week or more.

Materials suitable for decontamination of buildings are the same as those used in the field. A mixture of 50% chloride of lime and 50% water by weight is best.

Concrete or wooden floors readily absorb mustard and lewisite and should be covered with a layer of freshly prepared slurry by means of brooms and left for at least 24 hours. The slurry is then removed by scrubbing the floor with water (hot soapy water is preferable.) Badly contaminated floors and woodwork should be torn out and replaced with new structure if practicable.

Walls and ceilings of a building, if not too heavily contaminated with mustard, may be neutralized by spraying and swabbing with slurry, a mixture of 50% chloride of lime and 50% water by weight. The 3-gallon decontaminating apparatus (pressure type) is particularly suited for spraying walls and ceilings which cannot be reached with brooms or brushes. After 24 hours, the walls and ceilings should be washed with hot soapy water and the room or building aired for several hours. If mustard gas odors are still present, the decontamination process should be repeated.

If a building is contaminated with lewisite alone, it can be decontaminated with water, preferably with a high pressure hose. The resulting compound is an arsenic poison and must be washed away.

Heavily contaminated parts should be torn out and destroyed with fire. Mustard and lewisite soak into wood, plaster, wall paper, and concrete and are extremely difficult to eradicate. The vapor from the absorbed gas is given off for a long time after the surface layer is removed. It may help to coat the walls, ceiling and floor with a thin solution of water glass (sodium silicate) after surface decontamination. The water glass hardens and seals in the vapors, but this is not necessarily a permanent treatment, especially on floors where it will wear off.

Decontamination of Household Furnishings

Household furnishings made of fabric such as curtains, draperies, linens, and rugs which are easily removed may be destroyed by burning or burying or they may be decontaminated by the same methods indicated for clothing. Mattresses may be treated with steam in apparatus ordinarily used for disinfecting mattresses. This is effective for mustard. Since there is no record in the literature on the effect of steam on lewisite beyond simple hydrolysis, steam may be insufficient treatment in this case.

Upholstered furniture presents a difficult problem because the upholstery will soak up vapors of persistent gases as well as splashes of liquid agents. Decontamination is practically out of the question; hence, destruction by fire is normally carried out.

Kitchen equipment made of metal may be boiled in sodium sulfide or green solution or wiped off with kerosene followed by soap and water as described under machinery.

Decontamination of Machinery

Greasy or oily <u>metal</u> surfaces which have been contaminated with mustard or lewisite should first be cleaned with kerosene or gasoline. (Careful, fire hazard!) These solvents do not destroy the gases but dissolve them so that most of the poisonous material may be removed. The very thin coating of contaminant remaining is then destroyed with steam, bleach paste, hot sodium sulfide, or Green Solution. The latter two are less corrosive than the bleach. After such treatment the surface should be washed, dried, polished, and oiled. The rags used should then be burned.

Decontamination of Vehicles and Machinery

Vehicles or other machinery may be decontaminated on the outside by slurry, followed by washing with hot soapy water. Bleach should not be used on the motors of cars and other working parts because of its corrosiveness. Such parts should be treated in the same way as instruments, using alcohol or gasoline, hot water and soap, or such other non-corrosive material as may be provided to remove the gas. Upholstery and other absorbent parts when contaminated should be torn out and burned.

Decontamination of Clothing

Clothing may be contaminated by vesicant agents such as mustard and lewisite and rendered dangerous to wear, either through direct contact with the liquid substance or through exposure to the toxic vapor. Liquid mustard and lewisite will penetrate ordinary clothing very quickly. Severe burns will result unless the contaminated clothing is immediately removed, or the contaminated portions cut away, and unless first-aid treatment is applied immediately thereafter to the affected parts of the body.

In the case of exposure to mustard vapor, contamination is more gradual, the degree depending upon the concentration of the gas and the time of exposure. A very brief contact with mustard vapor might not cause contamination of clothing or produce a burn. On the other hand, clothing exposed to even a low concentration of mustard gas for 1 hour will be so contaminated that burns would probably result from wearing it.

In this connection, the highly insidious nature of mustard gas makes the protection problem a very difficult one. Vapor burns do not develop until several hours after contact and there is no pain or other immediate physicial indication of danger except the possible perception of the gas by its odor. The keenest sense of smell, however, gradually becomes fatigued by the odor of mustard gas so that after continued contact the odor may not be perceived at all.

It is evident that as a general rule of protection, whenever it is known that persons have been exposed to persistent gases they should be removed as soon as possible from the contaminated area. They should bathe with hot water and soap and put on fresh clothing if it is available. Otherwise their clothing should be decontaminated before it is worn again.

Clothing contaminated only by the vapors of mustard may be decontaminated by hanging up the garments so that they will be exposed to the sun and wind. In warm bright weather, two days' airing will generally be sufficient. Care should be taken not to hang garments close together, especially not on top of one another. In cool weather this method should not be relied on. Nor should this method be used in the case of lewisite contamination since moisture of the atmosphere will hydrolyze the lewisite and leave an insoluble residue which is still vesicant on contact with the skin.

A more positive method of destroying mustard gas in clothing is to subject it to steam. If contaminated with mustard vapor only, clothing may be decontaminated by such treatment in 2 hours. If splashed with liquid mustard it should be steamed for 4 to 6 hours.

There is no accurate information available on the effect of steam on lewisite except that it causes simple hydrolysis. Consequently steaming of clothing cannot be recommended until it has been proved that no toxic residue remains.

Various sorts of steam disinfectors can be improvised from materials available on the spot. The simplest is merely a large can provided with a false bottom. About 6 or 8 inches of water is placed in the can. The clothing is placed on the false bottom so that it does not touch the water. The can is covered but not so tightly as to prevent the escape of the steam. The capacity of such a disinfector can be increased by hanging additional clothing in an inverted canvas bag suspended over the can, the open end of the bag being tied about the sides of the can.

Steaming, especially for wollen clothing, is much preferable to boiling.

If a cylinder of chlorine and a suitable tube are available, the steam decontamination process can be accelerated. The clothing is hung in a suspended inverted canvas bag, the open end of the sack being tied or drawn together. Chlorine from the cylinder is run in at the top by means of a rubber tube or a pipe. The sack from time to time is shaken to insure contact between the chlorine and all the clothing.

Vapor-contaminated clothing should be treated with chlorine in this manner for 10 to 15 minutes and then steamed for half an hour. If splashed with liquid mustard the chlorine treatment should be given for 30 minutes followed by one hour's steaming.

If chlorine is used, it is essential that it be applied first and the steam afterward. If this process is reversed, results will not be satisfactory.

When clothing which has been splashed with liquid mustard gas is ... removed from the chlorine, a fine whitish crystalline substance will be seen on the cloth at the places where it was splashed. This substance is the reaction product of liquid mustard and chlorine and should be brushed off before the garments are steamed. If such a substance is noted when treating clothing which was believed to have been exposed to mustard vapor only, its presence is a certain indication that the clothing was actually splashed with the liquid agent. The clothing should then be treated accordingly.

A considerable amount of clothing may be treated with chlorine at one time if hung in a tightly closed room, tent, or dugout, in which chlorine can be released. This method should not be attempted without expert operators and unless there is no danger of persons in the vicinity being gassed when the enclosure is opened.

The method of sending men wearing gas masks into a chlorine chamber for chlorine treatment of the clothing they are wearing is not recommended. In no case should such a method be undertaken without supervision of an expert who is able to gauge and control the concentration of gas in the chamber. In any case, this method is not highly effective.

Another method of decontamination is to place the contaminated clothing in a receptacle containing a solution of sodium carbonate (soda ash, washing soda). The proportion should be ¼ lb. of soda to each gallon of water. This should be heated to about 80° C. (180°F) for about 2 hours. Do not allow to boil. Such treatment will cause some deterioration of woolen cloth but will not harm cotton. This method is effective for lewisite as well as mustard.

Little, if anything, can be done in the way of decontamination of shoes which are permeated with mustard. If the mustard has splashed only lightly and if it has not yet soaked into the leather, it may be neutralized by applying bleach or bleach paste. As a safety precaution it would be well for men subjected to mustard gas to shuffle their feet from time to time through a mixture of bleach and dry earth or sand. It is noteworthy that well-worn shoe leather absorbs mustard gas much more quickly than new.

Chloramine T, when available, is useful for the decontamination of clothing containing mustard since the reaction is milder. However, details of its use are not available. Higher cost is also a disadvantage.

Ordinary dry cleaning will not suffice for treating contaminated clothes.

Personnel engaged in decontamination of clothing should wear gas masks and protective suits. They should not touch contaminated garments with their bare hands.

Papers, Documents, etc.

Papers, documents, etc. may be stored in an enclosed space for several days and treated with gaseous ammonia to remove mustard gas. If soaking with water will not destroy them, 1% sodium sulfide for mustard and sodium carbonate solution for lewisite is more effective. Only very important paper articles should be decontaminated; others should be burned.

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OPERATIONS LETTER NO. 104

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Supersedes OCD Publication 2206, which was a tentative outline prepared for discussion at Gas Specialist Course at War Department Civilian Protection Schools

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TO: Regional Directors.

FROM: James M. Landis, *Director*.

SUBJECT: Duties of U. S. Citizens Defense Corps in Gas Defense.

SPECIAL DISTRIBUTION INSTRUCTIONS: To all State and Local Defense Councils. Attention: State Gas Consultants and Senior Gas Officers.

This operations letter details the duties of the State Gas Consultant, the Senior (local) Gas Officer and his staff, and describes the additional duties which units of the U. S. Citizens Defense Corps must assume in the gas protection program.

The duties before, during, and after a gas attack of all such personnel are as follows:

STATE GAS CONSULTANT

(Duties should be authorized under the authority of the State Defense Council)

Duties before gas attack:

1. Provide technical advice to State Defense Council in all matters relating to protection of civilians within the State against war gases.

2. Organize the State gas defense program and provide technical advice to Senior Gas Officers, through Commanders of the U. S. Citizens Defense Corps, in the organization of their local gas defense programs.

3. Make recommendations to the State Defense Council in regard to funds necessary for the organization and operation of the gas defense program, including a contingent fund for use in an emergency.

4. Plan the gas defense educational program for civilian protection personnel in cooperation with the U. S. Office of Civilian Defense, State and local authorities, and assist in its execution.

5. Determine the availability and location of all decontaminating materials.

6. Recommend technical qualifications and urge the appointment of qualified Senior Gas Officers by Commanders of the local U. S. Citizens Defense Corps.

7. Assist Senior Gas Officers, through local Commanders of the U. S. Citizens Defense Corps, to determine the amount and nature of necessary equipment and to procure it.

8. Inform Senior Gas Officers of the location of the Chemical Warfare Service or other laboratories where samples of gas are to be sent.

Duties during gas attack:

1. Be available for consultation with local Commanders and through them to Senior Gas Officers, by telephone or other method of communication.

Duties after gas attack:

1. Consult, through local Commanders of the U. S. Citizens Defense Corps, with Senior Gas Officers of attacked areas, to ascer-

tain effectiveness of gas protection program and modifications necessary for protection against future attacks. Receive reports from local Commanders and transmit reports to Regional Office of OCD.

Senior Gas Officer

(Duties should be authorized under direction of the Commander of the U. S. Citizens Defense Corps)

Duties before gas attack:

1. Develop and organize a gas defense program for the local community under the authority of the Commander of the U. S. Citizens Defense Corps. This will include appointment of necessary assistants as described in Operations Letter No. 91 (Operations Letter No. 42, Supplement No. 2).

2. Study the meteorological and topographical features of his area and their possible relationships to gas attack. This may be based on reports of gas reconnaissance agents.

3. Plan and execute a training program for the technical instruction of protection personnel actively concerned with gas defense in cooperation with the U. S. Office of Civilian Defense, State, and local authorities.

4. Make recommendations to the Commander in regard to funds necessary for the organization and operation of the Gas Defense Program, including a contingent fund for use in an emergency.

5. Determine the amount and nature of necessary equipment and supplies and arrange for their procurement and storage in appropriate locations and their issue to all services.

6. Arrange for issue of detector materials and instruct reconnaissance agents in placing indicators.

7. Develop lay educational programs to promote and maintain civilian morale, and educate the public in self-aid against gas with cooperation of the Chief of Emergency Medical Service (Operations Letter No. 46).

8. Arrange in cooperation with the Air Raid Warden Service for the development of an adequate gas alarm system and for the education of the public concerning recognition of such alarms.

9. Organize laboratory services for the detection and identification of war gases. This should be provided in cooperation with the Local Health Department as described in the section on Health Department.

10. Cooperate with and supply technical assistance to the Chiefs of the various services of the U. S. Citizens Defense Corps in organizing their services and training their personnel in gas defense.

11. Assign an Assistant Gas Officer to each divisional and district control center.

12. Assign Gas Reconnaissance Agents to each zone warden's post. The air-raid warden's zone is the area of operation of the Gas Reconnaissance Agent. Where warden zones have not been established according to OCD recommendations, one Gas Reconnaissance Agent should serve an area containing a population of approximately 25,000.

13. Supervise the Laundry Officer in the organization of facilities for the collection, transportation, decontamination or destruction, and redistribution of clothing.

Duties during gas attack:

1. Report at the main Control Center and serve as technical adviser in gas defense to the Commander and the individual services.

2. Recommend to the Commander the dispatching of a Gas Reconnaissance Agent from a zone warden post to area from which gas is reported.

3. On the basis of reports of the Gas Reconnaissance Agents, make decisions and advise in regard to:

A. Presence of gas.
B. Nature of the gas used.
C. Areas to be delineated, policed, and evacuated.
D. Areas requiring immediate decontamination, and the order of their priority.

4. Provide information to the Commander regarding the presence and location of gas and the integration of the activities of the various services concerned with gas defense.

Duties after gas attack:

1. Appraise and evaluate the extent and amount of contamination remaining, recommend to the Commander which areas should

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be decontaminated and the order of their priority and which should be left for weathering. Recommend when decontaminated areas may safely be opened for the public. This will be based on information supplied by the Gas Reconnaissance Agent.

2. Confer with Chiefs of all Services of the U. S. Citizens Defense Corps in order to determine the effectiveness of the protection provided to and by those services in the previous gas attack, and discuss plans for improvement of gas defense.

3. Make an inventory of the protective equipment available for use in future attacks and obtain additional equipment as necessary. Experience may require new items of equipment as well as replacements.

4. Obtain reports of laboratory analysis of gas samples and advise Health Department and other Services regarding action to be taken. Make certain that samples are forwarded to Chemical Warfare Service or other laboratory as necessary.

5. Integrate reports of gas reconnaissance agents and of other protection personnel in regard to gas incidents in a report for the Commander.

Assistant Gas Officers

Duties before gas attack:

Assist Senior Gas Officer in his several duties.

Duties during gas attack:

1. Report to divisional or district control center and serve in capacity similar to that of Senior Gas Officer at main control center.

2. Report periodically to Senior Gas Officer and obtain instructions from him.

Duties after gas attack:

Same as before.

Gas Reconnaissance Agent

Duties before gas attack:

1. Study the meteorological and topographical feature of his area and their possible relationships to gas attack.

2. Prepare painted surfaces and issue them to each sector post when ordered to do so by the Senior Gas Officer, and maintain them following distribution.

3. Acquaint himself with the air-raid wardens in the area and, upon their request, provide technical assistance to them in the instruction of residents in preparation against gas attack.

Duties during gas attack:

1. Report for duty at designated post.

2. When directed from Control Center, proceed to suspicious area, verify or disprove the presence of gas and identify any chemical agents with the assistance of chemical detectors.

3. Check and correct, if necessary, actions taken by air-raid wardens in regard to gas attack.

4. Make report of incident to the Control Center. Report should include a statement as to the presence or absence of gas, nature of gas, boundaries of contaminated areas, and recommendations for decontamination and evacuation.

5. Collect sample of gas for transmission to laboratory for analysis.

6. Check the posting of gas warning signs at contaminated areas.

7. Provide technical assistance to wardens on request in advising citizens in evading gas and the use of masks.

8. Assist in the control of panic.

9. Provide technical supervision of the emergency decontamination of the strategic areas as ordered from the Control Center.

Duties after gas attack:

1. Obtain information as to the extent and amount of contamination in his area and make written report to Senior Gas Officer.

2. Assist Senior Gas Officer in designating contaminated areas and in determining the areas to be decontaminated, the order of their priority, and the areas to be allowed to weather.

3. Under the authority of the Senior Gas Officer advise the air-raid warden as to the desirability of removing individuals from structures within the gassed area, and supply him with technical advice as to the means by which individuals may be removed.

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4. Inspect decontaminated areas, buildings, machinery, and vehicles (including chemical tests) to see that decontamination is adequate and recommend to the Senior Gas Officer the removal of restrictions.

Laundry Officer

Duties before gas attack:

1. Prepare plans under the supervision of the Senior Gas Officer for the collection, transportation, decontamination or destruction, and redistribution of clothing. This should include protective clothing.

2. Assist the Senior Gas Officer in educating the public in procedures for the home decontamination of clothing contaminated with vapor.

3. Supervise the training of personnel and the preparation of designated laundries to handle and decontaminate clothing, including protective clothing.

Duties during gas attack:

None.

Duties after gas attack:

1. Provide for the collection, transportation, decontamination or destruction, and redistribution of contaminated clothing. This should include protective clothing.

2. Decontamination of laundry interiors, trucks, and any other necessary areas or objects, under the supervision of the Chief of Public Works.

3. Assist civilian population in cooperation with air-raid warden in decontaminating clothing contaminated with vapor.

Commander

Duties before gas attack:

1. Plan with the technical assistance of the Senior Gas Officer for the changes that a gas attack would necessitate in operation of the protection services of a community.

Duties during gas attack:

1. Administer and coordinate defense against gas on the basis of the technical advice of the Senior Gas Officer.

Duties after gas attack:

1. Administer and coordinate defense against gas on the basis of the technical advice of the Senior Gas Officer and provide that such defense will be effective against future attacks.

Incident Officer

Duties before gas attack:

1. Under direction of the Commander acquaint himself with the duties and responsibilities of the Senior Gas Officer and Gas Reconnaissance Agents, and the special duties of all units of the Citizens Defense Corps during a gas attack.

Duties during gas attack:

1. With the advice of the Gas Reconnaissance Agent, regulate the scope of operations of the services present within the gassed area.

2. Consult with the Gas Reconnaissance Agent at the site of the incident, and assist the latter to establish "gas limits" (similar to fire lines) beyond which the public shall not approaach.

Duties after gas attack:

1. As a part of his report to the Commander, include a statement of the operations of the units present under conditions of gas exposure and recommend necessary changes to the Commander and Senior Gas Officer.

Air-Raid Warden

Duties before gas attack:

1. Store and care for his personal protective equipment.

2. Provide for a supply of water in sector post for emergency cleansing.

3. Advise residents of sector in regard to gas protection and use of gas masks.

4. Be familiar with gas protection plans of each household in sector.

5. Maintain a list at sector post of homes in sector to which persons needing self-aid may be admitted.

Duties during gas attack:

1. Place paint detector surface, distributed by Gas Reconnaissance Agent, outside the post at sound of air-raid warning.

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2. Suspect presence of chemical agent and report suspicion to the Control Center.

3. Don gas mask and sound gas alarm if presence of gas is strongly suspected and keep people indoors until danger has passed.

4. Rope off contaminated areas as delineated by Gas Reconnaissance Agent.

5. Inform Gas Reconnaissance Agent regarding the presence of people in buildings and assist in the removal of persons from buildings unsafe for occupancy.

6. With the technical assistance of a Gas Reconnaissance Agent advise citizens concerning the methods of evading gas and the use of a mask in the attack.

7. Direct contaminated persons to places in sector where they may administer self-aid.

8. Provide gas casualties with all possible assistance and treatment, including eye irrigation, without exposing himself to dangerous contamination.

9. Notify Control Center of occurrence of gas casualties.

10. On advice of Gas Reconnaissance Agent notify householders that it is safe to leave their homes after a gas attack.

11. Cleanse himself at sector post or other suitable location when necessary.

Duties after gas attack:

1. Check on materials available for protection against further attacks and obtain necessary replacements.

2. Assist Laundry Officer in the collection of contaminated clothing and its distribution after decontamination, and in the education of civilians in the handling and decontamination of clothing contaminated with vapor.

3. Assist persons returning to the sector after it has been decontaminated.

Police Services

Duties before gas attack:

1. Store and care for his personal protective equipment.

Duties during gas attack:

1. Police contaminated areas.

2. Assist in removing persons from areas designated by Commander on recommendation of Senior Gas Officer.

Duties after gas attack:

1. Police contaminated areas.

2. Assist in removing persons from areas designated by Commander on recommendation of Senior Gas Officer.

3. Assist in the reoccupation of decontaminated areas.

Fire Services

Duties before gas attack:

1. Store and care for his personal protective equipment.

Duties during gas attack:

1. Provide self-protection consistent with minimal interruption in fire defense.

2. Protect fire-fighting equipment against contamination.

3. Send contaminated vehicles and equipment vitally needed during the gas attack to vehicle decontamination facilities under supervision of public works.

4. Perform self-cleansing at cleansing stations or elsewhere when necessary.

Duties after gas attack:

1. Provide personnel and equipment for removing liquid contamination with water on request of Commander.

2. Check on materials and equipment available for protection against further attacks and obtain necessary replacements.

Emergency Medical Service

Duties before gas attack:

1. Plan with assistance of Senior Gas Officer for the establishment of gas cleansing stations for cleansing gassed patients with other injuries and for cleansing of civilian protection personnel. Each hospital of 150 beds or more should be provided with a cleansing station. Cleansing stations should be available in the ratio of one per 50,000 population and should be located at smaller hospitals or casualty stations where 150-bed hospitals are not available in this ratio.

2. Recruit, train, and assign personnel to gas cleansing stations for cleansing services.

3. Provide instruction, in cooperation with

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the Senior Gas Officer, for general public and civilian protection personnel in self-protection and self-cleansing (Operations Letter 46).

4. Provide for instruction of physicians in diagnosis and treatment of chemical casualties.

5. Assist hospitals in planning for handling of gas casualties.

6. Assure adequate distribution of protective clothing and gas masks and other protective equipment to members of mobile medical teams and train personnel in their use.

7. Make provision for training drivers of ambulances and sitting case cars in protection of their equipment against liquid-gas contamination; inform them of arrangements for vehicle decontamination by Emergency Public Works Service.

8. Arrange for the protection from contamination of the equipment used to transport contaminated casualties insofar as it is possible.

Duties during gas attack:

1. Upon advice of the Senior Gas Officer and under the orders of the Commander, man the gas cleansing stations.

2. Advise other services of the U. S. Citizens Defense Corps in regard to first-aid cleansing of their personnel.

3. Assign a mobile medical team to gas cleansing stations for first aid.

Duties after gas attack:

1. Evaluate the effectiveness of the cleansing procedures which have been used.

2. Provide follow-up treatment of patients.

3. Prepare inventory of protective equipment available for use in future attacks and obtain additional equipment as necessary.

4. Cleanse bodies of the dead to facilitate identification.

Local Health Department

Duties before gas attack:

1. Provide for analyses for war gases in samples of food and water. These tests may be performed in a local health department if laboratory facilities are adequate. In such case it is desirable to utilize the same laboratory facilities for the analysis for war gases of air and other materials. Where laboratory facilities other than those of the local health department are more suitable for use in the analysis of war gases, arrangements should be made by the local health department for the analysis of samples of water and food.

2. Advise the Senior Gas Officer regarding the nature of instructions to the public concerning precautions to be taken in the event of water-supply contamination. Such instructions are to be promulgated by the health officer.

3. Cooperate with waterworks officials in planning for the protection and decontamination of the water supply.

Duties during gas attack:

1. Collect samples of food and water for laboratory analysis if contamination is suspected.

2. Inform the public regarding contamination of food and water supplies, including recommendations in regard to self-protection.

Duties after gas attack:

1. Decontaminate, destroy, or otherwise provide for the handling and disposal of contaminated food supplies.

2. Assist the waterworks in the treatment of contaminated water supplies.

3. Advise the Senior Gas Officer in regard to the safety of the public water and food supplies and inform the public regarding contamination of such supplies, and methods of dealing with it.

4. Obtain reports of analyses of samples of water or food and take appropriate action. Save specimens of contaminated water and food for transmission whenever necessary to a Chemical Warfare Service or other laboratory, by the Senior Gas Officer.

Public Works

Duties before gas attack:

1. Organize decontamination squads.

2. Arrange for provision of decontaminating equipment and materials and for their storage and issue.

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3. Designate suitable filling stations and garages for decontamination of vehicles. Personnel of designated facilities may be enrolled in the decontamination service.

4. With advice of Senior Gas Officer train and instruct decontamination service personnel.

Duties during gas attack:

1. Perform emergency decontamination of critical facilities (e. g., hospitals), emergency vehicles (e. g., ambulances), areas where rescue is required, and vital machinery, according to priority as assigned by the Commander upon recommendation of the Senior Gas Officer.

Duties after gas attack:

1. Decontaminate streets, buildings, areas, machinery, and vehicles in the order of priority assigned by the Commander, upon recommendation of the Senior Gas Officer.

Public Utilities

(Including Public Transportation Services)

Duties before gas attack:

1. In consultation with Senior Gas Officer arrange for personal and collective protection of personnel required to operate vital facilities such as switchboards, power plants, pumping stations, and control centers.

Duties during gas attack:

1. Perform emergency decontamination of areas and objects whenever necessary to maintain or restore service.

Duties after gas attack:

1. Decontaminate public transport vehicles, equipment, and gassed areas in which utilities are to be repaired.

Transportation Services

(Including Drivers)

Duties before gas attack:

1. Store and care for his personal protective equipment.

Duties during gas attack:

1. Protect interior of vehicles and drivers against contamination insofar as possible.

2. Be on alert for contamination of vehicles and deliver contaminated vehicles which are immediately necessary to designated vehicle-decontamination facilities operated under supervision of public works.

Duties after gas attack:

1. Arrange return of vehicles after decontamination.

Emergency Welfare Services

Provide emergency food and housing for persons removed from contaminated areas. (This will not involve technical knowledge of chemical agents.)

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OFFICE OF CIVILIAN DEFENSE

WASHINGTON, D. C.

2 PAGES

Issued: January 20, 1943.
Effective: Immediately.

OPERATIONS LETTER NO. 106

To: Regional Directors.

From: James M. Landis, *Director.*

Subject: Care and Distribution of Gas Masks.

Special Distribution Instructions: State and local Defense Councils for the special attention of States and communities to which gas masks have been allocated.

Adult noncombatant masks are now being shipped from manufacturers and U. S. Office of Civilian Defense Supply Depots to communities which have received allocations of masks and have returned, properly executed, OCD Form No. 501. These will be in assorted sizes as follows: 9 percent large adult, 76 percent medium adult, and 15 percent child (small adult). Additional masks amounting to 5 percent of the total number allocated are being sent with each shipment for training use. The sizes of these will be assorted as follows: 25 percent large adult, 50 percent medium adult, and 25 percent child (small adult).

Valuable and critical materials are used in the manufacture of gas masks. Hence, care must be exercised in their handling, distribution, and storage in order that the usefulness of the present limited supply may be preserved as long as possible.

It is recommended that 5 percent of the masks other than those designated for training purposes be held in reserve by the Local Property Officer and that broken and defective masks and those with exhausted canisters be replaced from this reserve. It is recommended that the remainder, other than those designated for training purposes, be distributed to the protective services in communities, in accordance with "Regulations No. 1, Governing Loans of Equipment and Supplies to Civil Authorities" (paragraph 7c) approximately as follows:*

	Percent
Staff (Service Chiefs, Incident Officers, Senior Gas Officers, Gas Reconnaissance Agents, Chief Technical Intelligence Officer, Waterworks Officer and assistants, Health Officer and assistants, Messengers, Drivers, nonmedical)	12.5
Fire Service (Regular and Auxiliary Firemen)	10.5
Police Service (Regular and Auxiliary Policemen)	18.5
Air Raid Wardens Service (Wardens, Fire Guards)	30.0
Rescue Service	1.5
Medical Service (Member of Emergency Medical Field Units, Stretcher Teams, Ambulance and Sitting Case Car Drivers, Cleansing Station Personnel)	12.5
Public Works (Decontamination Personnel and other regular and emergency personnel required in gassed areas)	9.0
Public Utilities (all municipal and private utility personnel whose services are essential for emergency repairs in gassed areas or maintenance of operation of utilities during gas attack)	5.5

* These percentages are set forth as a rough guide in distribution. Variations may be necessary to suit local conditions.

It is recommended that approximately 20 percent of the number allocated to each service be stored by that service in places readily available to it, as for example, Police Stations, Fire Stations, Sector Wardens' Posts, Hospital and Casualty Stations serving as assembly points for medical teams, Rescue

Depots, Public Works, and Public Utilities Warehouse. *Storage must be in a cool, dry place and masks should be kept from contact with sunlight, oils, or corrosive liquids and vapors.* This increment of masks should be held as a reserve and should not be assigned to individuals. It is important that this reserve be decentralized as a safeguard against fire or bombing and also to permit rapid distribution in case of an emergency.

The remaining 80 percent allocated to the services may be issued to individuals in the services but should not be carried by them during their daily activities. These masks should be kept at the posts where the individuals will assemble during drills or enemy action. Under no circumstances should masks be assigned to individuals before they have received training in their use and care, including proper storage.

The Commander of the Local U. S. Citizens Defense Corps, through his Senior Gas Officer, should immediately arrange a gas mask training program for those to whom masks are to be issued. If no Senior Gas Officer has been appointed, steps should be taken to appoint one in accordance with Operations Letters 42 and 91. Training should follow the Outline for Gas Defense A in Office of Civilian Defense publication Training Courses for Civilian Protection. Protection Against Gas, also published by the Office of Civilian Defense, contains valuable information on training and maintenance.

In this training program, the Commander and Senior Gas Officer of the Local U. S. Citizens Defense Corps should utilize the services of individuals in the community who have attended the War Department Civilian Protection Schools. If there are no qualified individuals in the community, assistance should be sought from the State Gas Consultant who may, in turn, request aid from the Regional Director of the U. S. Office of Civilian Defense.

Repair of masks is not to be attempted locally except in case of extreme necessity. Broken and defective masks or those with exhausted canisters should be collected by the Local Property Officer and returned, preferably in lots of 20 or more, to the nearest U. S. Office of Civilian Defense Supply Depot listed below for repair and replacement:

- Salt Lake City, Utah: 341 Pierpont Avenue.
- Chicago, Illinois: 1750 Wrightwood Avenue.
- Fitchburg, Massachusetts: Willow Street.
- Hanover, Pennsylvania.
- Birmingham, Alabama: 503 South 22nd Street (Long Furniture Manufacturing Co.).

When a Local Property Officer has masks which he wishes to return he should so notify the nearest Depot Commander who will then send shipping instructions and a Government Bill of Lading which will authorize the transportation of the damaged masks without expense to the locality.

After use, masks should not be worn by another individual without proper sterilization. Instructions for sterilization are given in Office of Civilian Defense publication, "Protection Against Gas." In addition to formaldehyde, as recommended, certain germicides such as dimethyl benzyl alkyl ammonium chloride (sold under various trade names such as Roccal, Zephiran, etc.) or closely related neutral substances can be used for sterilization. Every mask must be sterilized by the trainee upon conclusion of the drill class and before the mask is returned to the instructor in charge.

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OFFICE OF CIVILIAN DEFENSE
WASHINGTON, D. C.

1 PAGE

ISSUED: April 8, 1943.
EFFECTIVE: Immediately.

OPERATIONS LETTER No. 124
(Supplement No. 4 to Operations Letter No. 42)

TO: Regional Directors.

FROM: James M. Landis, *Director*.

SUBJECT: Gas Cleansing Stations.

SPECIAL DISTRIBUTION INSTRUCTIONS: To State and Local Defense Councils and Hospital Administrators.

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1. In order to avoid confusion in use of the term "decontamination," it is recommended that the term be reserved for areas and objects and that hereafter the removal of vesicant liquids from persons be termed "gas cleansing." The facilities established for this purpose will be called "gas cleansing stations."

2. The primary purpose of these facilities is the protection of hospitals and casualty stations and their staffs and patients from contamination by injured persons who have been exposed to vesicant agents. Contaminated persons, including Citizens Defense Corps members, who are not disabled, are expected to cleanse themselves in nearby private homes or other local facilities.

3. In large cities in the target areas, it is recommended that cleansing stations be provided at or adjacent to hospitals in the ratio of one station for 50,000 inhabitants. A station should be provided at every hospital that has 150 beds or more, and if this does not bring the number up to the recommended ratio, additional stations should be established at smaller hospitals or casualty stations. At least one station should be established in every city of 25,000 or more in the target areas.

4. Under present conditions of scarcity of materials and manpower, construction of new facilities is generally not justified. Cleansing stations should be established in connection with casualty receiving hospitals by conversion of sufficient existing facilities to cleanse persons who are both injured and contaminated.

The necessity of using available establishments and materials and avoiding requests for priorities for construction of new facilities cannot be emphasized too greatly. Materials such as pipe, fittings, and shower heads must be obtained in the community from available stocks and from suppliers of used and reclaimed equipment.

5. The chief of Emergency Medical Service and the senior gas officer should assist hospital superintendents in planning their cleansing facilities. In hospitals the facilities which should prove suitable for conversion to cleansing stations, roughly in the order of preference, are hydrotherapy rooms, nurses' or internes' locker and shower rooms, part of the outpatient department, garages, or other separate structures. In the event these are not available, facilities must be arranged in nearby schools, gymnasiums, swimming pools, shower rooms, club houses, and community centers.

Plans should be fully made for immediate establishment and equipment of necessary gas cleansing stations in event of need. It is desirable that each large community establish without delay at least one gas cleansing station for training purposes.

6. Cleansing stations should be equipped to take care of one-third to one-half of the hourly casualty receiving capacity of the hospital to be served. The professional staff will consist of mobile medical teams assigned when the station is activated, supplemented by an additional staff of attendants to assist in undressing the injured, moving stretchers, caring for clothing and valuables, maintaining supplies, and dressing wounds. A detailed description of the operation of a typical gas cleansing station will be provided shortly as a Medical Division circular.

7. The local chief of Emergency Medical Service is responsible for the development of these stations. The senior gas officer of the community should act as his consultant in helping to establish these facilities. Industrial plants working on war contracts that wish to provide cleansing facilities for employees should be given aid and advice by the chief of Emergency Medical Service and the senior gas officer.

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OFFICE OF CIVILIAN DEFENSE

WASHINGTON, D. C.

1 PAGE

ISSUED: May 15, 1943.
EFFECTIVE: Immediately.

OPERATIONS LETTER No. 128

(SUPERSEDES OPERATIONS LETTER No. 46)

TO: Regional Directors.

FROM: James M. Landis, *Director.*

SUBJECT: How to Protect Yourself Against War Gas.

SPECIAL DISTRIBUTION INSTRUCTIONS: To State and local Defense Councils and all members of the Citizens Defense Corps, to supersede Operations Letter No. 46.

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1. Stay indoors. A tightly closed room affords protection against war gas. All windows and doors should be tightly shut, and blankets (to be soaked with water) or cardboard should be kept in readiness to cover and seal shattered windows. Choose a room on an upper floor if possible; most war gases are heavier than air, although they may be carried up with air currents.

2. If caught outdoors in a gas attack, get out of the area at once. Look down and shield your eyes with your arm. Do not worry about any brief vapor exposure to which you may be subjected. The danger from this source is not great.

3. Prompt action will avoid serious effects. If you know or suspect that you have gotten any of the gas on your person or clothing, do not go hunting for a casualty station or gas cleansing station and expect someone else to help you. *Knock on the first door* you come to, and take whatever steps are necessary. Self-aid is the quickest and safest way.

4. This is what you should do. This routine should be memorized so it will be done automatically in an emergency:

(*a*) *Remove shoes and outer clothing and drop them outside the house,* in a covered can if available. Do not touch this clothing again except with sticks or gas-proof gloves. Do not cling to false modesty. To enter a house with contaminated clothing endangers everyone in it.

(*b*) *Get to a bathroom, kitchen, or laundry room as fast as possible.*

(*c*) *If your eyes have been exposed to liquid gas or spray,* flush them immediately. Plain water out of a faucet, shower-head, canteen, or douche bag will do, but a lukewarm dilute solution of bicarbonate of soda (heaping tablespoonful in a quart of water) is even better, if it is handy. Let anyone nearby help you.

(*d*) *If drops of liquid blister gas have splashed the skin,* you can prevent serious burns by adequate cleansing. Promptly blot up the liquid with pieces of cleansing tissue, cloth, or a handkerchief, which should be disposed of carefully in order that it cannot contaminate anyone else. Then sponge the skin briskly with laundry bleach containing sodium hypochlorite, if it is at hand, and rinse off under the shower or in a tub. A thorough bath with a vigorous lathering is the final step, *which should never be omitted.* Dry the skin by patting. Do not rub. Dress in whatever clean clothing you can get. If blisters develop, you should seek medical advice.

(*e*) *If your nose and throat feel irritated,* snuff and gargle with a dilute solution of bicarbonate of soda. If your chest feels heavy and oppressed, if you have any trouble breathing, or if smoking becomes distasteful, lie down immediately and stay perfectly still until you can be taken to a doctor. Do this even if you feel fine otherwise.

5. Remember: Cleanse yourself quickly and calmly. Follow the instructions of your air-raid warden.

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